REFINER
AND NATURAL GASOLINE MANUFACTURER
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# Research Is Good Insurance

THE well conducted research department is insurance against ruinous inter-industry competition of the future. It is the best form of protection against stagnation, and stagnation in industry usually spells insolvency.

During "times like these" one of the initial steps in retrenchment made by manufacturing companies is to reduce the research appropriation. Some companies go further and abolish their research divisions. It is all very well to clean house, to study the endeavor of the research, its scope and possible application of results, to re-arrange routine and concentrate effort, but to strangle research, to abolish it, is a peculiar form of misappropriation of funds likely to prove more damaging than the passing of dividends.

Companies do not provide themselves with a research department like the buying of a new cracking unit. It is the product of growth, of evolution—becoming more valuable, more efficient, only through experience. Strike it down and in its place there grows an incoherency and lack of interest, felt and understood by all workers in the organization from executive to foremen, through recognition of the fact that the company lacks the leadership of the research department to which it has looked for new development.

Studies of developments in other fields are essential for often there is more competition between industries than between companies in the same industry. Without an efficiently functioning research department where is there any insurance against losses in this type of modern competition? When the research department is seriously impaired then the insurance on the future of the company is reduced in proportion.

# Physical and Chemical Uniformity

A HIGHER degree of fractionation is possible and ultimately may prove profitable. Its application would assist in securing more uniform motor fuels for national distribution.

Constant uniformity of physical properties of motor fuels is being rapidly approached. Chemically, motor fuels differ, and this difference is brought about by the composition of the natural crude gasoline, the cracked or synthetic gasoline, and the operating methods of refiners. Chemical uniformity is perhaps impossible of attainment, but it can be more closely approached than is at present the case.

Recent practice in analysis makes possible the selection by fractionation of those "bands" of constituents in a given distillate which contribute to the low known rating of a motor fuel. Equipment can be provided at the refinery for the extraction of these "bands" of knocking hydrocarbons. Waste heat can be utilized for much of this type of fractional distillation. Chemical uniformity will be more nearly secured when the chemicals of motor fuels are extracted if they knock, or retained in the distillate if they are satisfactory performers.

These "bands," chemically constructed so that they are unfit for motor fuel, can be isolated—perhaps marketed as solvents or special products—or they can be reformed by cracking, again fractionated for removal of any remaining undesirable "bands," and blended into the finished product.

Future specifications might be written to designate quantities by percentage of paraffins, aromatics, unsaturates, permissible in a given motor fuel. The lack of chemical uniformity of gasolines constitutes the major factor in the securing of uniform performance. The cracking process, fractionation and re-fractionation, extraction and remixing, will assist in securing that uniformity so needed by the automotive industry.

# *Transition . . .*

# Is Keynote in Motor Fuel History

GEORGE REID
*Associate Editor*

STATISTICAL history often makes dry reading. It becomes alive, however, when interpreted in in the light of future development. Motor fuel history is worthy of continued study inasmuch as it shows a transition in manufacturing methods. Most pertinent is the fact that the transition must continue. Motor fuel statistics will in the future show the further effects of this transition through the increases in production of synthetic motor fuels by the refining industry.

Seven years ago, as shown in Table 1, the cracking unit yielded 26.4 per cent of the industry's motor fuel production, while crude oil contributed in the form of natural yield by skimming operations,, 66 per cent of the motor fuel. During 1931, the production of cracked gasoline reached 40.8 per cent of the total, while the natural straight run production dropped to 51 per cent. During the same period gasoline recovery from the barrel of crude increased from 32.4 per cent in 1925 to 44 per cent in 1931.

The contributing factors forcing the industry into ever more utilization of the rapidly developing cracking process are the facts that refining is hardly profitable without the increased recovery of motor fuel available through its use, and the increasing difficulty experienced in the sale of straight run gasoline. Fuel oil and distillate markets have been more or less glutted with subsequent low prices, for the past few years and there is little to indicate a revival of demand sufficient to offset the advantages of cracking such products into motor fuels. Further, the automotive industry continues to request an ever increasing volume of higher anti-knock value fuels with which to operate its present day motors and those designed for future distribution.

Gasoline production this year has been at the approximate rate of 25 per cent straight run and 20 per cent cracked gasoline from the barrel of crude run to refineries, which indicates a condition of unbalance, for certainly to meet the demand for motor fuels of high octane rating under existing marketing methods and requirements, the industry must produce at least as much cracked gasoline as it does straight run. Definitely established trends point to a future condition where the petroleum refining industry will of necessity produce more synthetic motor fuel than natural—and such yields prevail now in three refining districts.

It appears that the industry requires the cracked gasoline yield from an operating total of around 150,000 barrels cracking unit charging capacity, above that capacity now in service and operating. And this additional capacity, involving construction of from 30 to 50 new units, will only offset the difference in production of cracked gasoline necessary to reach a balance between natural and synthetic motor fuels. It in no way indicates a limit of new cracking unit application, for the yield of synthetic fuels must continue to increase—and a production from the industry of 50 per cent straight run and 50 per cent cracked gasoline will not enable it to meet marketing requirements from the standpoint of volatility and anti-knock rating. The industry requires from 50 to 75 modern, large capacity cracking units each year to offset the decrease in capacity brought about through dismantling of obsolete and unsafe cracking equipment. Between 30 and 35 units are known to have been erected or announced so far this year, for example, and perhaps as many more have

**TABLE 1**

**Seven years of Motor Fuel History showing the relation of Straight-run, Cracked, and Natural Gasoline***

| Year | Total Gasoline Barrels | Total Cracked-Gasoline Bbls. and pctge | Total Natural Gasoline Bbls. and pctge. | Total Straight Run Gasoline Bbls. and pctge. |
|---|---|---|---|---|
| 1925..... | 259,601,000 | 68,583,000<br>26.4 | 19,636,000<br>7.6 | 171,382,000<br>66 |
| 1926..... | 299,734,000 | 93,736,000<br>31.3 | 27,696,000<br>9.24 | 178,302,000<br>59.5 |
| 1927..... | 330,435,000 | 101,226,000<br>30.7 | 32,162,000<br>9.7 | 197,047,000<br>59.6 |
| 1928..... | 376,945,000 | 122,554,000<br>32.6 | 35,223,000<br>9.4 | 219,168,000<br>58.0 |
| 1929..... | 434,241,000 | 143,759,000<br>33.2 | 45,463,000<br>10.4 | 245,019,000<br>56.5 |
| 1930..... | 436,217,000 | 164,243,000<br>37.4 | 46,670,000<br>10.6 | 225,304,000<br>51.6 |
| 1931..... | 431,560,000 | 176,181,000<br>40.8 | 35,116,000<br>8.1 | 220,263,000<br>51. |
| Month of March, 1932 | 31,789,000 | 13,381,000<br>42.1 | 1,920,000<br>6. | 16,488,000<br>51.9 |

*Source—Bureau of Mines Annual and Monthly Petroleum Reports.

***THE trend of compression ratios in the automotive industry is higher.***

***Compression ratios can be stepped up to 7 to 1 without meeting with serious difficulty.***

***To secure performance with low weights the motor industry wishes to advance compression ratios.***

***Higher compression ratios are interpreted in terms of higher octane numbers for motor fuels.***

***Application of cracking must continue to secure the present high octane values and those of the future.***

***The possibility of a carburetor substitute for internal combustion engines will not retard cracking.***

been erected, or are planned, concerning which no reports have been made.

The foregoing discussion applies only to the industry as it operates in the United States. Foreign refining has begun feeling the effects of the transition from skimming to cracking, and although ultimate acceptance and application of American refining methods is certain, such application may come about more slowly.

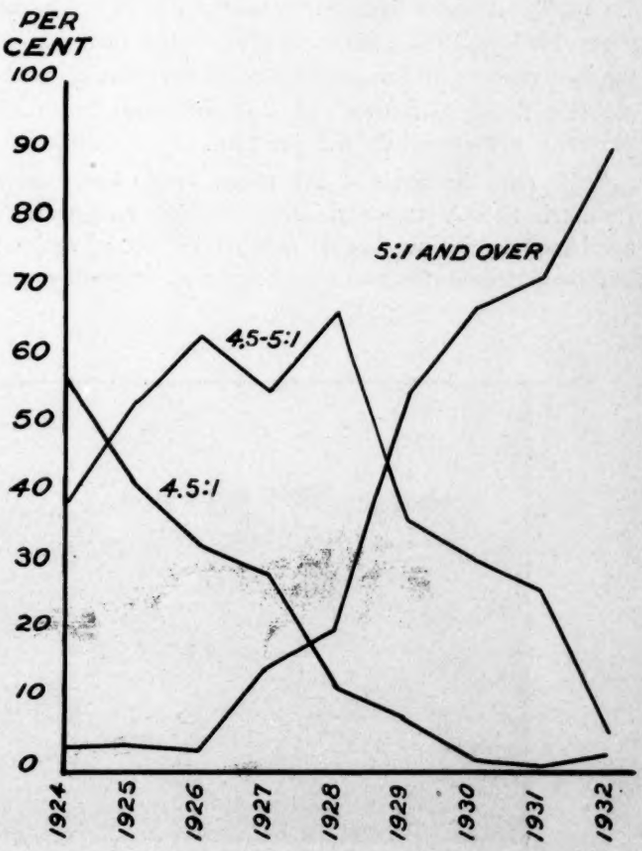
Production of motor fuel in the United States during the first three months of this year has been in the order of 20 per cent synthetic and 24 per cent natural gasoline from the crude charged to stills. A finer degree of accuracy can not be determined for the reason that a number of companies, because of the bug-a-boo of cracking patent litigation, do not report either number and type of cracking units, nor volume of cracked gasoline production. The proportions, however, are indicative of unbalance both for present day market requirements and the known needs of the future.

While some authorities have expressed views contrary to the trend toward increasing cracking and naphtha reforming, and contrary to the known needs and future requirements of the automotive industry, the opposite is true. Investigation into the matter discloses the fact that automotive engineers wish to proceed to still higher compression ratios and they continue to express their need for more uniform fuels of higher octane number. Since 1923 THE REFINER AND NATURAL GASOLINE MANUFACTURER has advised the more widespread utilization of the cracking process. Especially during the past three or four years has this advocacy been vigorous (see references), for the reason that the handwriting on industry's wall has definitely pointed to increasing demand for better fuels, and for more efficient operation in the plant, and for conservation—perhaps of a selfish nature, for fuel oil and distillate prices for the most part have been indicative of the fact that it is more profitable to convert the larger proportion of such products into motor fuel.

## COMPRESSION RATIOS

Factors, and important ones, at work in the automotive industry necessitate continued increase in compression ratios. Principally the industry is confronted with the task of providing increasingly better automobiles of lower weight and lower price. Lacking the higher compression ratios the performance of present day cars might have been secured through greater displacement —and this means that larger and heavier engines would be required—which in turn means heavier parts, more weight, in the rest of the automobile assembly. This method of approach is all right in so far as the high priced automobile is concerned. However, the market for automobiles is in the low-priced field, totaling about 85 per cent at present and while a return of "good times" may tend to lower this percentage, the low-priced field always has and always will be the larger proportion of that industry's business.

It is not possible with low-weight small cars to secure greater horsepower, rapid acceleration, high speed, and other desirable features of performance and economy without high compression ratios. In securing performance with the small car better than that of large cars of five years ago the automotive industry has created a demand for premium motor fuels—gasolines of higher octane number. Ninety per cent of cars for 1932 dis-




***Compression Ratio of Motor Cars Based on Number of Models Offered***

tribution have compression ratios of 5 to 1 and over. Five years ago this percentage was 21. Automotive engineers have pretty well agreed that compression ratios can be above 7 to 1 with modern engines before serious difficulties are encountered. Certainly this indicates a future raising of octane rating of motor fuels, and future application of the cracking process.

Dr. Gustav Egloff, Universal Oil Products Company, before the Western Petroleum Refiners Association this spring, stated that the gasoline appetite of today's automobile engine has changed radically, and the need for meeting this changed condition satisfactorily has given rise to new and keener competition in the oil industry in furnishing high anti-knock gasoline. Dr. Egloff concluded his discussion of the utilization of the cracking process for securing anti-knock gasoline from various grades and types of cracking unit charging stock, with a discussion of the needs of the automotive industry and the trend toward higher compression ratios. He says in part:

"Increase in the octane number of gasoline is being made imperative by the motor car manufacturers who are continually stepping up the compression ratios of their engines. The pressure they are exerting upon the oil industry for higher anti-knock gasoline is best illustrated by showing the American passenger car engine trends by the per cent of motors (put out as new models) having compression ratios less than 4.5 to 1, 4.5 to 5 to 1, and those at or above 5.0 to 1 for the years 1924 to 1932. Most striking is the fact that in the last nine years the percentage of cars having compression ratios of 5.0 to 1 or over, increased from 3.5 per cent of the total to 91.5 per cent.

"The data in Table 4 are taken from Automotive Industries, 1932, statistical issue. The percentages here are based on the number of new model motor cars put out by the manufacturers each year as to number of cylinders, bore, stroke, displacement and compression ratios.

"Plotting percentages of each group against the year, the curves clearly show the decline of lower compression ratios and the rapid climb of those models having compression ratios of 5.0 to 1 or higher."

There has been some discussion recently of developments in the automotive industry which point to the possible elimination of the carburetor. This is especially interesting because motor fuel specifications are limited or governed by this fuel mixing device, and if it is to be eventually abandoned, gasoline specifications will naturally be altered, which in turn would alter some of the manufacturing processes in the refining industry.

A. Ludlow Clayden, Sun Oil Company, before the recent convention of the National Petroleum Association, outlined something of the developments along such lines. After discussing the use of a multiple of carburetors (perhaps one to each cylinder) Mr. Clayden stated "The next step, mechanically, is to abandon the carburetor and to inject fuel either into the entering air stream or directly into the cylinder during the intake stroke. This introduces the very large difficulty of accurately metering extremely small volumes of liquid, but notwithstanding this very major mechanical problem it does seem quite likely that this will prove to be the ultimate answer. Such mechanical developments, however, are fairly far in the future. Meanwhile the volumetric efficiency can be very much improved and the distributional irregularities of manifolds substantially reduced, if fuels of much higher volatility become generally available. The development of some fuel feeding system other than the carburetor and manifold may come much faster than at present appears likely. Should it do so we will not have a near future demand for gasolines of higher volatility. However, nobody knows how great an improvement might result from the designing of automobile engines to use only fuel of very

***Hydrogenation Plant in Operation at the Bayonne, New Jersey, Refinery of Standard Oil Company of New Jersey***

high volatility, and nobody knows how difficult it is going to be to create a substitute for the carburetor. The direction in which engineers will move is very likely to be influenced by the action of refiners. If gasoline volatility shows signs of improving very rapidly, then one line would be encouraged. If it does not do so the engineers' tendency will be to follow the other line.

In an article, "Solid Injection—A Look Into the Future of Motor Fuels," by Earl Petty, appearing in these columns (April, 1932, page 277-280), the new type of carburetor substitute was presented in detail, with results published which were taken from a series of tests, over a period of a year, in connection with the operation of motor cars, trucks, busses, and exhaustive work with airplane engines. In concluding, Mr. Petty stated, "It will be readily seen that the various demonstrations begin to upset a number of specifications (motor fuel), requirements aand characteristics about which the entire refining industry has been developed, viz.: control of boiling ranges, fractionation, per cent of fraction for motor fuel, and stabilization. What might a device of this kind mean to the refining industry if it would suddenly appear as standard equipment on all automobile and airplane engines? There is enough of its shadow already visible and coming from research and development laboratories of the automobile accessory industry to warrant careful consideration and study."

Certainly it is true that such a transition from carburetor to carburetor substitute might be made by the internal combustion engine industry. Research and experimentation is more widely under way than is generally understood and doubtless more shall be heard of such devices in the near future. However, regardless of the developments in this direction, the refining industry must continue to provide the powerful fuels which it can derive from its heavier distillates by cracking. Specifications may change, in time, and requirements not be so exacting, but the yield of motor fuel per barrel of crude will not be influenced. The production of motor fuel, scientifically, and with greater economy, depends upon the consistent and constant improvement in the cracking art.

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Cracking Capacity Increased During Year—Reid. July, 1929, page 61.
Anti-Knock Motor Fuel Demand Responsible for Growth in Cracking—Reid. July, 1929, page 63.
Large Construction Program Justified—Reid. July, 1929, page 100.
Survey of Cracking Capacity of United States—Reid. July, 1929, page 108.
Further Expansion of Refining Facilities Indicated—Reid. February, 1930, page 74.
Few Concerns Dominate Refining Capacity—Reid. September, 1930, page 100.
More Cracking Units, Less Straightrun Gasoline—Reid. January, 1931, page 68.
Cracking Capacity Continues to Increase—Reid. January, 1931, page 71.
High Quality Motor Fuel Demand Indicates Cracking Expansion—Reid. May, 1931, page 97.
Technical Expansion—Reid. August, 1931, page 79.
More Cracking and Reforming Units Indicated—Reid. December, 1931, page 104.
Refining in 1932—Reid. January, 1932, page 1.
Octane Requirements Forcing Cracking Expansion—Reid. April, 1932, page 274.
Integrated Units Controlling More Refining Capacity—Reid. May, 1932, page 324.


**TABLE 2**

**Crude Oil Charged to Still, Gasoline Produced, and Increase in Recovery Over a Period of Seven years***

| Year | Barrels Crude to Stills | Gasoline Yield from Crude Bbls. | Percent Gasoline Recovery |
|---|---|---|---|
| 1925 | 739,920,000 | 239,965,000 | 32.43 |
| 1926 | 782,561,000 | 272,038,000 | 34.76 |
| 1927 | 828,835,000 | 298,273,000 | 36.0 |
| 1928 | 913,295,000 | 341,722,000 | 37.4 |
| 1929 | 987,708,000 | 388,778,000 | 39.36 |
| 1930 | 927,447,000 | 389,547,000 | 42.00 |
| 1931 | 894,608,000 | 396,444,000 | 44.1 |
| March, 1932 | 68,502,000 | 29,869,000 | 43.6 |

*Source—Bureau of Mines Annual and Monthly Petroleum Reports.

**TABLE 3**

**Gasoline Production—Straight-run and Cracked* Jan., Feb., Mar., 1932**

*From Bureau of Mines Monthly Petroleum Statements.

Percentage of Crude Run

| | Straight-run | | Cracked | |
|---|---|---|---|---|
| | Barrels | Percent | Barrels | Percent |
| January, 1932 | 16,629,000 | 24.2 | 13,981,000 | 20.3 |
| February, 1932 | 15,780,000 | 24.7 | 13,598,000 | 21.3 |
| March, 1932 | 16,488,000 | 24.1 | 13,381,000 | 19.5 |

**TABLE 4**

**American Passenger Car Engine Trends**

**Number of Cylinders**

(Based on number of models offered)

| Year | 4 Cyl. % | 6 Cyl. % | 8 Cyl. % | 12 and 16 Cyl. % |
|---|---|---|---|---|
| 1924 | 19.5 | 70.3 | 10.2 | ..... |
| 1925 | 14.8 | 67.8 | 17.4 | ..... |
| 1926 | 13.00 | 66.0 | 21.0 | ..... |
| 1927 | 6.00 | 65.0 | 29.0 | ..... |
| 1928 | 6.50 | 58.0 | 35.5 | ..... |
| 1929 | 4.00 | 55.00 | 41.00 | ..... |
| 1930 | 2.92 | 43.20 | 52.70 | .98 |
| 1931 | 3.85 | 30.80 | 61.50 | 3.85 |
| 1932 | 4.20 | 30.60 | 54.20 | 11.0 |

**Bore, Stroke, Displacement**

(Based on number of models offered)

| Year | Bore, inches | Stroke inches | Piston Displ. cu. in. |
|---|---|---|---|
| 1924 | 3.43 | 4.81 | 258.1 |
| 1925 | 3.48 | 4.73 | 262.6 |
| 1926 | 3.37 | 4.72 | 260.59 |
| 1927 | 3.26 | 4.67 | 254.86 |
| 1928 | 3.27 | 4.58 | 257.73 |
| 1929 | 3.27 | 4.57 | 261.27 |
| 1930 | 3.260 | 4.51 | 264.59 |
| 1931 | 3.21 | 4.45 | 273.00 |
| 1932 | 3.28 | 4.41 | 283.93 |

**Compression Ratio**

(Based on number of models offered)

| Year | Less than 4.5 to 1 % | 4.5-5.0 to 1 % | 5.0 to 1 and over % |
|---|---|---|---|
| 1924 | 57.7 | 38.8 | 3.5 |
| 1925 | 42.1 | 53.9 | 4.0 |
| 1926 | 33.3 | 63.6 | 3.1 |
| 1927 | 28.9 | 55.3 | 15.8 |
| 1928 | 12.0 | 67.0 | 21.0 |
| 1929 | 8.0 | 37.0 | 55.0 |
| 1930 | 2.1 | 31.3 | 66.6 |
| 1931 | 1.3 | 26.7 | 72.0 |
| 1932 | 2.8 | 5.7 | 91.5 |

# *Problems of*

# • Liquefied-Gas Industry

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**A LARGE number of papers have been published in recent years dealing with the various problems related to the properties, manufacture, handling, and utilization of liquefied gases. No attempt is, therefore made in this paper to cover any one subject in a comprehensive manner, but the paper is confined to a brief discussion of some basic economic considerations and a condensed review of some interesting technical problems encountered in the manufacture and utilization of liquefied gases.**

MID-YEAR MEETING
TULSA, JUNE 1, 2, 3, 1932

THE recent growth of the liquefied-gas industry is closely related to the adoption of rectification in the manufacture of natural gasoline. It will be of interest, therefore, to review briefly the purpose of rectification. It may be defined simply as the replacement of high vapor-pressure constituents by a larger, volume of fractions of lower vapor pressure, to obtain any desired effective volatility within the limits of a fixed vapor-pressure specification of a finished gasoline. These relations are illustrated in Figure 1, giving the relative volumes of different constituents of natural gasoline that may be substituted for each other without a change in the vapor pressure of the finished blend.

It will be noted that, with a motor gasoline having a vapor pressure of 10 pounds per square inch at 100° F., elimination of one volume of propane will permit substitution of 3.3 volumes if *iso*butane, or 4.85 volumes of normal butane, with a net gain in production of 2.3 and 3.85 volumes, respectively, and a corresponding improvement in effective volatility as regards ease of starting, acceleration, etc. Aside from these economic relations, there is no inherent objection to the inclusion of propane in a motor gasoline, but evidently substitution of butane for propane is desirable as long as butane for this purpose is available.

Removal of one volume of *iso*butane permits, with the same motor gasoline, substitution of 1.45 volumes of normal butane, with a net gain of only 0.45 volumes. While inherently desirable, rectification for the purpose of substituting normal for *iso*butane may, therefore, in many instances prove uneconomical.

If a surplus of natural gasoline is available, rejection of butane will, of course, permit inclusion of a larger percentage of natural gasoline in motor gasolines. A curve is included, Figure 1, giving the substitution value for butane of a typical natural gasoline of 24 pounds per square inch Reid vapor pressure. For a motor gasoline of 10 pounds per square inch vapor pressure, removal of one volume of butane will permit inclusion of about 3.05 volumes of natural gasoline. Since the butane content of such a gasoline will be slightly over 30 per cent, the three added volumes will contain nearly one volume of butane. The net result from substituting three volumes of natural gasoline for one volume of butane in that case is the substitution of two volumes of butane-free natural gasoline; in other words, the surplus natural gasoline would have to be rectified first for complete removal of butane before it could be utilized under these conditions.

Since the substitution value of butane for propane is 4.85, the substitution value of this typical natural gasoline for propane would be 3.05×4.85=14.8. Rectification for removal of propane is, therefore, one of the most effective steps for increasing the potential demand for natural gasoline. Every natural gasoline manufacturer who ships a gallon of propane to a refiner may destroy thereby substantially the potential demand for 15 gallons of natural gasoline of representative quality.

From this brief review of the economic relations underlying rectification certain general conclusions may be drawn as regards the potential supply of liquefied gases. Propane may definitely be classified as a liquefied gas. Butanes are potential liquefied gases only to the extent to which they cannot be utilized in motor gasolines, or for uses in which a price can be paid for them at least equal to that of motor gasolines. Otherwise their inclusion in motor gasoline is preferable, both because of their desireable effect on volatility and on detonation properties. Improvements in automotive design for control of vapor locking and better balance between supply and demand for petroleum products will, therefore, pro-

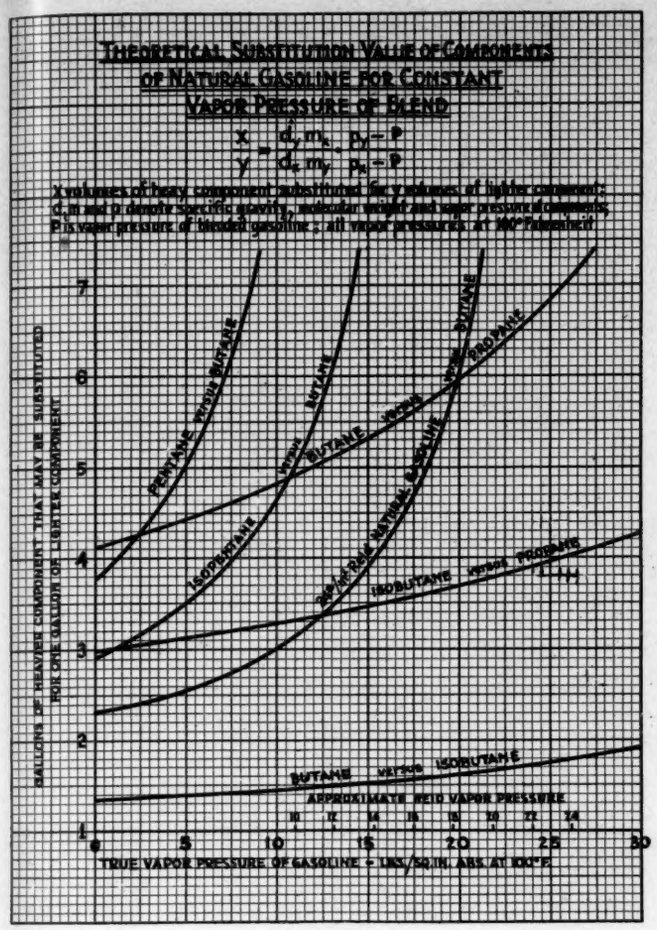



**FIGURE 1**
***Miscellaneous Problems Related to Liquefied Gasses***

bably lead to an increased utilization of butanes, perhaps both normal butane and *iso*butane, in motor gasolines and a corresponding curtailment of their use in liquefied gases. This contingency may as yet be remote, but it is reasonable to anticipate a trend in this direction.

## RECOVERY OF LIQUEFIED GASES INCIDENTAL TO NATURAL GASOLINE PRODUCTION AND EXTRACTION BEYOND THIS LIMIT

In estimating the potential production of liquefied gases, a clear distinction must be made between the amount that may be recovered incidental to the extraction of natural gasoline from the gas, and the extraction of liquefied gases beyond this point. In the latter case all charges for increased plant facilities, increased labor, commodities, etc., must be charged against the liquefied gas exclusively, with the result that the cost of extraction may become prohibitive. These relations are best illustrated by a specific example.

It shall be assumed that production of a natural gasoline having a normal butane content of 30 per cent is desired, from a gas having the following composition:

| | Gallons Per 1,000 Cubic Feet |
|---|---|
| Propane content | 1.9 |
| *Iso*butane content | 0.45 |
| Butane content | 0.80 |
| *Iso*pentane and heavier | 1.25 |

For the analysis of the problem, the conception of an "absorption factor" presented in a previous paper by the author[1] will be useful.

It was shown there that the absorption-plant requirements for the extraction of individual constituents may be defined by a factor proportional to absolute absorber pressure multiplied by the oil circulation in gallons per 1,000 cubic feet and divided by the vapor pressure of the individual constituents at absorber temperature. It was proved that a factor of about 1.3 is required for substantially complete extraction of any constituent, and that for factors less than unity the ratio between amount extracted and amount available in the gas is equal to the absorption factor. If the absorption factor for normal butane is known for any given set of operating conditions, the factors for propane, *iso*butane, and *iso*pentane may be obtained by multiplying the butane factor by 1/4, 2/3, and 2 2/3, respectively. This brief summary will serve for an approximate analysis of the present problem.

1. *Plant operated for gasoline extraction only.* It will be desirable in that case to recover substantially all fractions including, and heavier than *iso*pentane, represented by 1.25 gal. per 1000. Since a finished gasoline of 30 per cent butane is desired, the total gasoline production will amount to $\frac{1.25}{0.70} = 1.785$ gal. per 1000; or it will be necessary to extract 0.535 gal. per 1000 of butane. This represents $\frac{0.535}{0.800} = 0.675$ of the available butane content.

The plant will have to be operated, therefore, at a butane absorption factor of at least 0.675. To allow for variations in operating conditions, etc., the assumption will be made that actually a factor of 0.75 be employed. In that case extraction will be as shown in Case 1.

The amount of liquefied gas indicated by this analysis, viz., 0.29 gallons per 1000 butanes and 0.36 gallons per 1000 of propane is, of course, not available in finished form. It is partly contained in the raw gasoline, partly in various plant vapors; but the first step, viz., extraction from the natural gas, has been accomplished incidental to gasoline manufacture. Recovery of further amounts of liquefied gas beyond this quantity will involve considerable in-

[1] Alois Kremser, "Theoretical Analysis of the Absorption Process," Proc., Nat. Gasoline Assoc. of America, 9th annual convention (May 1930).

**CASE 1**

| | Absorption Factor | Extraction Efficiency | Gallons per 1,000 Extracted | Used in Gasoline | Available for Liquefied Gas |
|---|---|---|---|---|---|
| Propane | 0.19 | 0.19 | 0.360 | .... | 0.360 |
| *Iso*butane | 0.50 | 0.50 | 0.225 | .... | 0.225 |
| Butane | *0.75* | 0.75 | 0.600 | 0.535 | 0.065 |
| *Iso*pentane and heavier | 2.00 | 1.00 | 1.250 | 1.250 | .... |
| Total | | | | 1.785 | 0.650 |

**CASE 2**

| | Absorption Factor | Extraction Efficiency | Gallons Per 1,000 Extracted | Used In Gasoline | Available for Liquefied Gas | Gallons Per 1,000 Increase Over Case No. 1 |
|---|---|---|---|---|---|---|
| Propane | 0.36 | 0.36 | 0.685 | .... | 0.685 | 0.325 |
| *Iso*butane | *0.95* | 0.95 | 0.428 | .... | 0.428 | 0.203 |
| Butane | 1.43 | 1.00 | 0.800 | 0.535 | 0.265 | 0.200 |
| *Iso*pentane and heavier | 3.80 | 1.00 | 1.250 | 1.250 | .... | .... |
| Total | | | | 1.785 | 1.378 | 0.728 |

**CASE 3**

| | Absorption Factor | Extraction Efficiency | Gallons Per 1,000 Extracted | Used In Gasoline | Available for Liquefied Gas | Gallons Per 1,000 Increase Over Case No. 2 |
|---|---|---|---|---|---|---|
| Propane | *0.95* | 0.95 | 1.81 | .... | 1.81 | 1.125 |
| *Iso*butane | 2.51 | 1.00 | 0.45 | .... | 0.45 | 0.022 |
| Butane | 3.80 | 1.00 | 0.80 | 0.535 | 0.265 | .... |
| *Iso*pentane and heavier | 10.10 | 1.00 | 1.25 | 1.250 | .... | .... |
| Total | | | | 1.785 | 2.525 | 1.147 |

creases in plant size and operating costs, an important consideration from the viewpoint of costs.

2. *Plant operated for extraction of* 95 *per cent of available* iso*butane.* The plant will have to be operated at an *iso*butane absorption factor of at least 0.95, as shown in Case 2.

To extract the additional 0.728 gallons per 1000, it is necessary to increase the size of plant at the ratio of absorption factors, i. e., $\frac{1.43}{0.75}=1.91$ times, as compared to case No. 1, or the plant must be nearly doubled. The additional capacity represented by 0.91 units is required for extraction of 0.728 gallons per 1000, or amounts to $\frac{0.91}{0.728}=1.25$ units per gallon as compared to $\frac{1}{1.785}=0.56$ units per gallon of natural gasoline in case No. 1. The relative size of plant per gallon of additional liquefied gas is, therefore, 1.25.

$\frac{}{0.56}=$ *2.23 times* that per gallon of natural gas. While costs will not be in direct proportion to plant size, it will be apparent that the unit cost of the additional production is likely to be higher than for the extraction of natural gasoline.

3. *Plant operated for extraction of 95 per cent of available propane.* The plant will have to be operated at a propane absorption factor of at least 0.95, as shown in Case 3.

Compared to case No. 1, the plant size is increased at the ratio $\frac{3.80}{0.75}=5.06$. The increase over case No. 2 is, therefore, 5.06—1.91=3.15 units, or represents $\frac{3.15}{1.147}=2.75$ units per additional gallon. The plant size per gallon is, therefore, $\frac{2.75}{0.56}=$ *4.90 times* that per gallon of natural gasoline, a condition that should be reflected in a marked increase in unit costs.

It will be apparent from these relations that a careful analysis will be required in every individual case to determine the economic limit to which extraction of liquefied gases may properly be carried. As a broad generalization it may probably be stated that extraction of these products beyond the limit obtained incidental to manufacture of natural gasoline is likely to prove uneconomical, a fact that has not been given adequate weight in many estimates of potential supply.

The gas analysis used in the previous example has been chosen to represent approximately the average quality of natural gas produced in California. From the computed extraction figures, and the average gas production of California for the past year, which is

estimated as about 1050 million cubic feet per day, the following approximate estimate of the potential supply of liquefied gases may be derived:

**POTENTIAL CALIFORNIA PRODUCTION OF LIQUEFIED GASES**

| | (1) Incidental to Gasoline Manufacture | (2) Additional Beyond (1) by Substantially Complete Recovery of Butanes | (3) Additional Beyond (2) by Substantially Complete Propane Extraction | Total |
|---|---|---|---|---|
| | (Gallons Per Day) | | | |
| Propane ..... | 380,000 | 340,000 | 1,180,000 | 1,900,000 |
| *Iso*butane..... | 235,000 | 210,000 | 20,000 | 465,000 |
| Butane ..... | 70,000 | 210,000 | ..... | 280,000 |
| Total ..... | 685,000 | 760,000 | 1,200,000 | 2,645,000 |
| Relative plant size per gallon ..... | 1.00 | 2.23 | 4.90 | |

From the previous discussion it has been concluded that perhaps only the quantities indicated in the first column may be considered as economically recoverable. Even this volume consisting of 380,000 gallons per day of propane and 305,000 gallons per day of butanes is not available in liquid form, but consists largely of plant vapors commingled with relatively large amounts of methane and ethane. Special facilities for condensing and rectifying the desired products are, therefore, required. The installation of such special facilities can generally be justified only in plants where relatively large amounts of butanes and propane are available. For this reason the economically available supply is much less, perhaps less than 50 per cent, of the amounts given in the first column, or possibly not more than 10 per cent of the theoretical supply as determined by gas analysis.

The figures for California conditions are presented with the reservation that the estimate for the average composition of gas may be considerably in error. Nevertheless, the general conclusions would be equally applicable, even if the gas had an appreciably different composition.

Finally, it will be of interest to determine approximately the effect of raising the vapor pressure of motor gasolines. The average production of motor gasolines in California during 1931 amounted to about 190,000 barrels of 42 gallons each per day. An increase in the Reid vapor pressure of 2 pounds per square inch would have permitted the inclusion of about four per cent more butanes, or of about 320,000 gallons per day. Such a diversion of butanes to motor gasolines would greatly reduce the volume of butanes economically available for liquefied gases. This conclusion is of particular interest, because an increase in vapor pressure of the magnitude indicated is not only possible but altogether probable. These figures also serve to illustrate the fact that economic gains of considerable magnitude will result from the control of vapor locking by improvements in motor car design.

## MANUFACTURE AND UTILIZATION

The manufacturing process for liquefied gases involves a series of fractionating steps. In our plants the raw gasoline is processed first in a primary rectifier from which a butane-free overhead is taken. The bottoms from this unit, which contain a small percentage of propane, are separated in a secondary rectifying column into finished natural gasoline and an overhead cut consisting substantially of butanes.

The overhead from the primary column is condensed, passed to a water separator, and charged to the top of a so-called weathering column, which may be of some interest. It serves a three-fold purpose; control of vapor pressure, rectification, and partial dehydration. These results are accomplished in a rather simple manner by introducing the cold feed to the top of a 12-plate column, which is operated at a constant pressure and a thermostatically-controlled bottom temperature. No reflux is supplied, but a substantial degree of rectification is obtained due to the temperature differential between top and bottom of the column. The product leaving the column has a constant vapor pressure corresponding to the temperature and pressure existing at the bottom. Some typical operating conditions are: pressure 250 pound per square inch gage, feed temperature 75° F., bottom temperature 125° F. The performance of the column may be estimated from the following analyses:

| | Feed Volume, Vapor (Per Cent) | Product Volume, Liquid (Per Cent) |
|---|---|---|
| Methane ..... | 7.300 | ..... |
| Ethane ..... | 11.200 | 2.000 |
| Propane ..... | 87.500 | 98.000 |
| Water content, per cent by weight . | 0.017 | 0.003 |

The yield of finished product to feed under these conditions amounts to about 70 per cent, as compared to a theoretically possible yield of 87.5 per cent, for complete removal of ethane by rectification. The performance of this weathering column is, therefore, very satisfactory, especially in view of the very simple design, possibility of utilizing exhaust steam, absence of reflux equipment, etc. This same type of design has been utilized also with considerable success as a substitute for rectification in small gasoline plants, for the removal of fixed gases from crude and similar applications.

The product from the weathering column is then passed through a chemical drier, followed by a filter, and finally to storage. The chemical drier consists

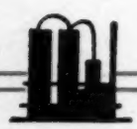
of a drum filled with quick lime, designed for convenient replacement of the charge. The flow of liquid is from bottom to top. The amount of water that has to be removed is relatively small and, consequently, the life of a charge is long. The water content of the final product is approximately 0.001 per cent by weight. Calodorant, a special odorizing agent developed by our company, is introduced into the discharge line to the storage tanks in a proportion of 0.5 gallons per 1000 gallons.

In a plant operated on this basis two primary products, one consisting substantially of butanes and the other almost pure propane, are obtained. From these products a variety of final blends of different propane and butane content are made, the composition depending on the desired specifications.

With bottled gas, control of the water content of the product is very important, to avoid freezing difficulties in service. It is impossible to present within the scope of this paper a full discussion of this subject, but it may be of interest to mention that, in addition to the steps described above, we have found it necessary to arrange for absolute drying of new cylinders, drying of gas used in testing cylinders, special precautions in handling empty cylinders, etc., to maintain the water content within permissible limits. Fortunately, the equilibrium relations between water and propane are such that water originally present in a cylinder will be depleted rather rapidly in normal service if the cylinder is re-filled with a dry product. Nevertheless, to maintain a water content consistently below 10 parts per million—the limit that we consider essential for cold weather service—requires careful attention to every phase of operations.

In the utilization of liquefied gases, especially bottled gases, the major technical problem was the development of suitable equipment, such as gas ranges, water heaters, etc., which would be properly adapted to the efficient use of the product. The cost per unit of heating value is necessarily high as compared to other fuels. A high thermal efficiency of the equipment is, therefore, one of the most effective means of reducing the service cost. Equipment sold for service with our liquefied gases must be submitted, therefore, to approval tests in our laboratories. If efficiency and other service characteristics are found adequate, the equipment is placed on our approved list. This policy involved considerable expenditures, but in cooperation with manufacturers a wide range of appliances which are now considered satisfactory has been developed. It has probably been one of the most important contributing factors to the gratifying growth of our liquefied-gas business.

This brief of some phases of the liquefied-gas industry will serve to emphasize the fact that the growth and continued success of this industry will depend to a large extent on a proper conception of its economic relations to other activities of the petroleum industry and on careful attention to the manifold technical problems arising in the manufacture, handling, and utilization of liquefied gases. The potential supply of these products, in spite of the economic limitations pointed out in the earlier part of the paper, is adequate to justify determined efforts directed towards expansion of this industry, especially in fields in which liquefied gases do not have to compete on a thermal basis only, but in which they are of especial merit due to their particular properties.



*Relation of . . .*

# C. F. R. Knock Ratings to Behavior of Fuels in Service

***Report of the Detonation Sub-committee of the Cooperative Fuel Research Committee.***

**T. A. BOYD**

***General Motors Corporation***
***Detroit, Michigan***

MID-YEAR MEETING
TULSA, JUNE 1, 2, 3, 1932

ONE of the most important points about any laboratory-testing method, as well as one of the principal problems of most of them, is the matter of getting the results of test to conform to those obtained in service. It was for this reason that, immediately following the development of a common apparatus and method of making laboratory knock ratings and the adoption of a uniform scale for expressing anti-knock quality,[1] the detonation sub-committee was instructed by the Cooperative Fuel Research Committee to undertake a comprehensive study of the matter of relating knock ratings, as made by the C. F. R. apparatus and method, to the actual road performance of fuels in automobile engines.

A considerable amount of past experience on the part of various men, obtained incidentally in connection with the development of knock-testing methods, had indicated that at the time of their tests the agreement between behavior in service laboratory ratings as made by the apparatus and method in use was reasonably good, at least for conventional gasolines as available up to that time. The tests, upon which the observation as just made were based, were conducted for the most part by members of the sub-committee. They were not, however, conducted in a cooperative or an official manner by the sub-committee as a whole, and in no case was use made of the complete C. F. R. knock-testing unit as finally agreed upon in a tentative way. Naturally, it was first necessary to have a uniform apparatus and procedure by which the laboratory test results of the various cooperating members could be obtained on a comparable basis before laboratory results could be compared with behavior in service in a cooperative or a comprehensive manner.

## AVAILABLE DATA ACCUMULATED

One of the first things done by the sub-committee when it began the investigation of this problem last fall was to request laboratories which happened to have made comparisons of labortary knock ratings with behavior in service—whether represented on the sub-committee or not—to report to the sub-committee such results as they might have. As a consequence of this request, a considerable amount of valuable data was received. These results came mainly from six laboratories. The conclusions reached independently by each of the six, as compiled by D. B. Brooks of the U. S. Bureau of Standards, who analyzed the reports, are given below. First, however, it should be said that in these tests each laboratory followed its own plan or precedure, and that the objective of the tests was not always the same. Hence, the results are not strictly comparable in every instance:

*Laboratory M*—The fuels used by this laboratory all contained tetraethyl lead; hence the conclusions reached apply only to this type of fuel. The conclusions are that the majority of cars rate fuels differently than do laboratory test engines; that the latter do not agree with one another; that an increase in jacket temperature or use of a richer mixture ratio improves the correlation of laboratory and road tests.

*Laboratory N*—The deductions drawn were that laboratory and road tests of cracked leaded fuels disagree, and that varying the mixture ratio used in the road tests did not eliminate the discrepancy—the presumption being that change of some factor other than mixture ratio would improve the correlation quite materially.

*Laboratory O*—As a result of comparing laboratory ratings on three types of detonation test engines with road results, it was concluded that no marked superiority was shown by any of the three, the agreement between the laboratory engines being much closer than that of the road test cars. A conclusion drawn from another series of tests was that there is not constant difference between road and laboratory ratings of cracked as compared with leaded fuels.

*Laboratory P*—No deductions.

*Laboratory Q*—The conclusion drawn is that oc-

[1] T. A. Boyd, "The Cooperative Fuel Research Apparatus and Method for Knock Testing," Proc., Twelfth Annual Meeting, Amer. Pet. Inst., Sect. III, p. 46 (1931).

tane numbers correlate very closely with road tests, and that "maximum knock as reported in the laboratory is a good average of all conditions and as close to any evaluation by ear on the road."

*Laboratory R*—The purpose of this laboratory's tests was to determine whether high anti-knock non-leaded fuels showed lower effective knock rating in service than leaded fuels of similar knock rating in the laboratory. The conclusion reached was that there was no substantial difference in the road performance of the two types of fuel.

## CONCLUSION

In briet, three of the laboratories find no substantial difference—larger than the experimental error—between laboratory and road tests; while the other three find differences too large to be accounted for solely by error. Leaded-cracked, straight-run, and California fuels are found in each category.

Now the conclusions from these tests, so concisely put by Mrs. Brooks, appear to show: first, that in cars some fuels rate the same in anti-knock quality—within the limits of ability to determine it—as they rate by conventional laboratory technique; and, second, that in other cases, or under other conditions, there are discrepancies between laboratory knock ratings and behavior in service. All of the work reported was carefully done; and, in spite of the fact that all results did not agree, it appears likely that the data are not in conflict. The results reported by some of the investigators suggest that, of the differences between the tests of the various investigators, one of the most outstanding is the composition of the fuels used in making the comparisons. That is to say, some of the investigators reported that in the cases of some fuels there are discrepancies between the ratings made in laboratory knock-testing engines and those made in automobile engines; while other fuels do not show such discrepancies. Consequently, unless both used the same fuels (which the laboratories participating in the above-mentioned tests did not), it would easily be possible for one investigator to find a discrepancy between the laboratory and the road, and for another to find none. And this was the case in the instance of the reports to which reference has just been made.

## PLANS FOR INVESTIGATING THE PROBLEM

At the time of the receipt of the reports in December of last year, as mentioned above, a special group from the sub-committee was appointed to prepare a program of investigation of this factor to be carried out under the direct auspices of the sub-committee. Such a program was settled upon at the meeting of the sub-committee held at the end of January of this year. In brief, this program consisted of two parts, as follows:

1. A series of cooperative road tests in cars on the part of several members of the sub-committee, to compare the car ratings of a number of selected fuels with conventional C. F. R. ratings. This group, hereafter called the "road test sub-committee," was asked, when selecting fuels for their tests, to choose some that are of the type on which discrepancies between C. F. R. ratings and behavior in service have been reported by different investigators and some of the type on which no disparity in cars has been reported.
2. Investigations to be made in the laboratory by individual members of the sub-committee, to evaluate the effects on the ratings of various types of gasolines of the changing of different conditions with respect to the C. F. R. knock-testing apparatus and method of test.

Meanwhile, at the January meeting of the sub-committee, progress reports on further investigations independently conducted by different members of the sub-committee indicated two things, as follows:

1. That, by comparison with a fuel consisting of an equal mixture of reference fuels "A-2" and "B-2" of the Standard Oil Development Company, both alone and treated with lead, some gasolines rated lower in automobile engines than they did by current C. F. R. procedure; that the amount of the differential between laboratory rating and behavior in service varied from one fuel to another, but that for the limited number of cars tested each fuel showed approximately the same average departure (if any) from the laboratory rating in each one of the cars.[2] The magnitude of this departure varied up to the equivalent of about 10 octane units.
2. That by making suitable changes in testing technique, it appears to be possible with the present C. F. R. knock-testing apparatus to get relative ratings on any given set of fuels which agree with the average behaviors of the given fuels in any given automobile engine.

## FIRST REPORT OF ROAD TEST SUB-COMMITTEE

The special road test sub-committee mentioned above presented its first progress report at a meeting of the sub-committee held April 6. They reported the results of an extensive series of comparative tests on six gasolines. The six fuels selected by the members of the sub-committee and used in their tests ranged in octane number from 68 to about 77. They may be described as follows:

a. A straight-run California gasoline, reference fuel "B-2" of the Standard Oil Development Company.
b. A blend of 3 cc. of lead tetraethyl per gallon

[2]Upon extending the number of cars tested, these invetigators later found that for any given gasoline the amount of the average differential between the laboratory rating and tendency to knock in service was not the same for every car.

in reference fuel "A-2" of the Standard Oil Development Company.

c. A vapor-phase cracked naphtha.

d. A liquid-phase cracked naphtha.

e. A vapor-phase cracked naphtha.

f. A 40 per cent blend of 1 deg. benzol in reference fuel "A-2."

For the purposes of the tests, these fuels were given symbols, such as "RT-1," "RT-2," etc., so that the compositions of the fuels might not be known to the operators of the cars. It should be said that the symbol numbers do not apply in numerical sequence to the fuels in the above list.

The method of test used consisted of matching each of the fuels in the various automobiles with blends of reference fuels "A-2" and "C-5" of the Standard Oil Development Company. (The octane number of reference fuel "A-2" is 48, and that of reference fuel "C-5" is approximately 77). The matching was carried out so that the fuel under test fell between a reference fuel mixture of higher knock value and a mixture of lower knock value than the unknown fuel, but the bracket between these two mixtures was not greater than the equivalent of 5 octane units. All results were reported in terms of the percentage of reference fuel "C-5" in the mixture of reference fuels "A-2" and "C-5" required to match the fuel under test. Speed was used as the criterion rather than intensity of knock; since the former was found to give definite data, and the latter decidedly indeterminate results. For instance, having determined the speed at which knock stopped using the unknown fuel, the percentage of reference fuel "C-5" corresponding to the unknown fuel was calculated by interpolation from the speeds found when knocking stopped with blends of the reference fuels as indicated above. To aid in interpreting the results of the tests, it may be said that a 4 per cent in the proportion of reference fuel "C-5" represents a change equivalent to about 1 octane unit according to the C. F. R. procedure.

The data secured in the tests by the several members of the group are tabulated in Table 1, each value given there being an average of several check runs. Some of the tests were made on steep hills, some on level roads, and some on chassis dynamometers. The tests included a variation of procedure, so that in some instances the car speed was accelerated until the knock stopped; while in other cases the engine speed was decelerated until the knock commenced.

The data of Table 1 are shown graphically, and, accordingly, in a much more easily read manner in Fig. 1. One important thing should be kept in mind in interpreting these data. This is that they represent only a progress report, and do not in any sense constitute final results.

**TABLE 1**

**Tabulation of Results Secured in First Series of Car Tests by the Special Sub-committee on Road Test Procedure**

(The Data Given are in Percentages of Reference Fuel "C-5" (Approximate Octane Number 77) Required to be Added to Reference Fuel "A-2" (Octane Number 48) to Match the Fuel Under Test).

| Test Unit | Laboratory | Fuel RT-1 | RT-2 | RT-3 | RT-4 | RT-7 | RT-8 |
|---|---|---|---|---|---|---|---|
| G.F.R. | A,B,C,D,E, | 86 | 72 | 100 | 102 | 83 | 84 |
| Buick, 6-30 | B | 70 | 66 | 80 | .. | .. | .. |
| | B | 67 | 44 | 92 | 72 | 67 | 92 |
| | D | 28 | .. | 53 | 42 | .. | .. |
| | D | 47 | .. | .. | 44 | .. | .. |
| | D | 44 | .. | 58 | 60 | .. | .. |
| | D | 47 | .. | .. | 60 | .. | .. |
| Buick, 8-32 | A | 50 | 62 | 67 | 63 | 71 | 88 |
| | B | 54 | 63 | 77 | .. | .. | .. |
| | B | 70 | 72 | 82 | 82 | 48 | 73 |
| | C | 67 | 73 | 79 | 79 | .. | .. |
| | C | 55 | 73 | 76 | 76 | 60 | 85 |
| | C | 20 | 74 | 60 | 83 | 61 | 91 |
| | D | 47 | .. | 53 | 57 | .. | .. |
| | D | 39 | .. | 56 | .. | .. | .. |
| | D | 66 | .. | .. | .. | .. | .. |
| | D | 52 | .. | .. | 60 | .. | .. |
| | D | 45 | .. | 54 | .. | .. | .. |
| | D | 43 | .. | .. | 70 | .. | .. |
| | D | 48 | .. | .. | .. | .. | .. |
| | D | 51 | .. | .. | 43 | .. | .. |
| Chevrolet, 6-31 | D | 44 | .. | 55 | 55 | .. | .. |
| | D | 50 | .. | .. | 55 | .. | .. |
| | D | 50 | .. | 70 | 55 | .. | .. |
| Chevrolet, 6-32 | A | 66 | 67 | 75 | 80 | 86 | 91 |
| | C | 66 | 74 | 84 | 90 | .. | .. |
| | C | 61 | 74 | 86 | 84 | 77 | 100 |
| | C | 55 | 80 | 85 | 87 | 63 | 100 |
| | E | 74 | 73 | 103 | 93 | 82 | 80 |
| Chrysler, 6-30 | A | 71 | 70 | 90 | 91 | 53 | 77 |
| Chrysler, 8-31 | D | 72 | .. | 81 | .. | .. | .. |
| | D | 66 | .. | 81 | 93 | .. | .. |
| | D | 77 | .. | 83 | .. | .. | .. |
| | D | 88 | .. | .. | 92 | .. | .. |
| | D | 91 | .. | 94 | 100 | .. | .. |
| | D | 85 | .. | .. | .. | .. | .. |
| Chrysler, 8-32 | A | 71 | 81 | 83 | 93 | 50 | 96 |
| | A | .. | .. | .. | .. | 61 | 88 |
| | B | 80 | 76 | 86 | .. | .. | .. |
| Auburn, 8-31 | B | 56 | 65 | .. | 84 | .. | .. |
| Ford, 4-31 | D | 29 | .. | 43 | 72 | .. | .. |
| | D | 46 | .. | 53 | 70 | .. | .. |
| | D | 64 | .. | 66 | .. | .. | .. |
| LaSalle, 8-30 | C | 75 | 66 | 77 | 81 | 40 | 100 |
| Packard, 8-29 | C | 20 | 70 | 63 | 57 | 55 | 81 |
| Packard, 8-32 | B | 75 | 74 | 79 | .. | .. | .. |
| Studebaker 8-30 | E | 70 | 72 | 85 | 85 | 56 | 65 |

## INTERPRETATION OF CAR TEST DATA

One of the most outstanding things about the data of Figure 1 is the wide variation in ratings obtained on any one fuel in a given make of car. These variations existed both when ratings were made by different laboratories using a different technique, and when they were made by the same laboratory using the same technique, but on repeating the tests on different days. The variations sometimes amounted to as much as the knock equivalent of 8 to 10 octane units.

The fuels themselves as rated by the conventional C. F. R. procedure varied in octane number from 68

for "RT-1" to about 77 for "RT-4," a total range of 9 octane numbers. So it was that the range of ratings of any one fuel obtained in any one car sometimes varied by as much as the total range for all the fuels tested.

On account of this relatively wide range in the ratings which they found on the road in different cars, and even in the same car from time to time, the special sub-committee on road test procedure felt that, in the light of their present knowledge, it is not as yet possible for a one-cylinder engine test procedure to be settled upon which will give results that correlate with service behavior for all cars. Consequently, the sub-committee pointed out the great need for developing a uniform technique for making road tests—one that will give results which are at once reasonably representative and uniform. Once it has been established what a representative average road rating is, then it appears that the C. F. R. procedure can be modified to give that rating. And so, at its own suggestion, the sub-committee was authorized to devote further attention to this important matter of road test procedure.

## ANALYSIS ON BASIS OF AVERAGES

From the data in Table 1 and Figure 1, D. B. Brooks has tabulated the average rating obtained for each one of the fuels on all cars, as follows:

| Fuel | C. F. R. Rating Minus Average Car Rating in Per Cent C-5 in A-2 | Average Difference Between C. F. R. and Car, Expressed in Equivalent Octane Units, Basis 4 Per Cent C-5 Equals Approximately 1 Per Cent Octane |
|---|---|---|
| RT-1 | 28.8 | 7.0 |
| RT-2 | 0.8 | 0.2 |
| RT-3 | 26.0 | 6.0 |
| RT-4 | 29.0 | 7.0 |
| RT-7 | 21.5 | 5.0 |
| RT-8 | —4.4 | —1.0 |

The above results show that, *on the basis of average ratings,* two of the fuels ("RT-2" and "RT-8") showed behaviors in cars which were in fair agreement with their respective ratings by the C. F. R. procedure; but that four of the fuels ("RT-1," "RT-3," "RT-4," and "RT-7") on the other hand, knocked worse in cars than in the laboratory engine by the equivalent of from 5 to 7 octane units. This is the thing which by some has been referred to as the discrepancy factor. Cases of some other types of gasoline have been observed, and independently reported to the subcommittee, in which the discrepancy between the rating in the laboratory and that obtained in cars has consisted not in the car rating being lower than the laboratory rating, but higher. However, whichever occurs, the results observed appear to be an indication that present C. F. R. procedure does not conform closely enough to the conditions under which automobile engines are run in service to give results which approximate average car behavior in the cases of some gasolines, although it does very well in the cases of other gasolines.

With regard to the actual magnitude of the average results reported above, however, mention is again made of the important fact that they constitute nothing more than preliminary data. For the present, therefore, they should be considered as qualitative rather than quantitative in character.

## VALIDITY OF OCTANE NUMBER NOT AFFECTED

It is important to note that none of the discrepancies reported invalidate in any sense the fundamental concept of octane number. Octane number is a universal language for expressing knock ratings obtained under certain specified conditions—under conditions which are uniform and carefully controlled. Strictly speaking, no other rating is an octane number. The conditions under which the octane numbers of fuels are now determined may not be right for all fuels, and apparently they are not; i. e., the conditions existing in laboratory tests are apparently not nearly enough like those which prevail in cars in service. However, that is not the fault of the octane number scale. The setting up of correct conditions under which to determine octane numbers is the problem now before the sub-committee.

## STUDIES OF DIFFERENT OPERATING CONDITIONS FOR C. F. R. UNIT

The second phase of the work of the sub-committee consists of experiments in the laboratories of individual members, to evalute the effects on the ratings of various types of fuels of changing different operating conditions on the present C. F. R. apparatus. The primary purpose of the road tests discussed above is to determine what ratings should be obtained. The purpose of the laboratory studies is to determine how such car ratings (when their proper values shall have been arrived at on the basis of comprehensive road tests) can be obtained with C. F. R. apparatus.

Accordingly, the various laboratories are studying the C. F. R. apparatus and method, to determine in a systematic and comprehensive manner the effects upon the ratings secured for fuels of various types of making changes in such representative factors as the following: speed, jacket temperature, mixture temperature, mixture ratio, spark setting, throttle opening, valve timing, turbulence, exhaust backpressure, and degree of scavenging, as well as various minor changes in the design of the engine and intake system. In addition to the investigation of the effects of making changes in one of the mentioned variables at a time, the different laboratories are experimenting also with making simultaneous changes in more than one variable. And it is this latter which has been found most effective in influencing the ratings obtained on fuels which in service depart from the conventional labora-

## RELATION BETWEEN C.F.R. KNOCK RATING AND CAR RATING FOR SIX DIFFERENT FUELS

SIX DIFFERENT REPRESENTATIVE GASOLINES DESIGNATED BELOW AS RT-1, RT-2, RT-3, RT-4, RT-7 AND RT-8 WERE COMPARED WITH BLENDS OF TWO STANDARD REFERENCE FUELS DESIGNATED AS C-5 AND A-2 IN BOTH THE C.F.R. ENGINE OPERATED IN ACCORDANCE WITH THE PRESENT STANDARD PROCEDURE FOR KNOCK TESTING AND IN THE AUTOMOBILES SHOWN BELOW

THE VERTICAL BARS INDICATE THE RANGE IN RATINGS THAT WAS OBSERVED FOR EACH MAKE OF CAR AND THE HEAVY HORIZONTAL DASHES (–) INDICATE EACH OBSERVATION. THE DATA OBTAINED BY EACH OF THE FIVE CO-OPERATING LABORATORIES ARE SHOWN BY THE LETTERS A, B, C, D AND E, RECORDED BESIDE EACH OBSERVATION.

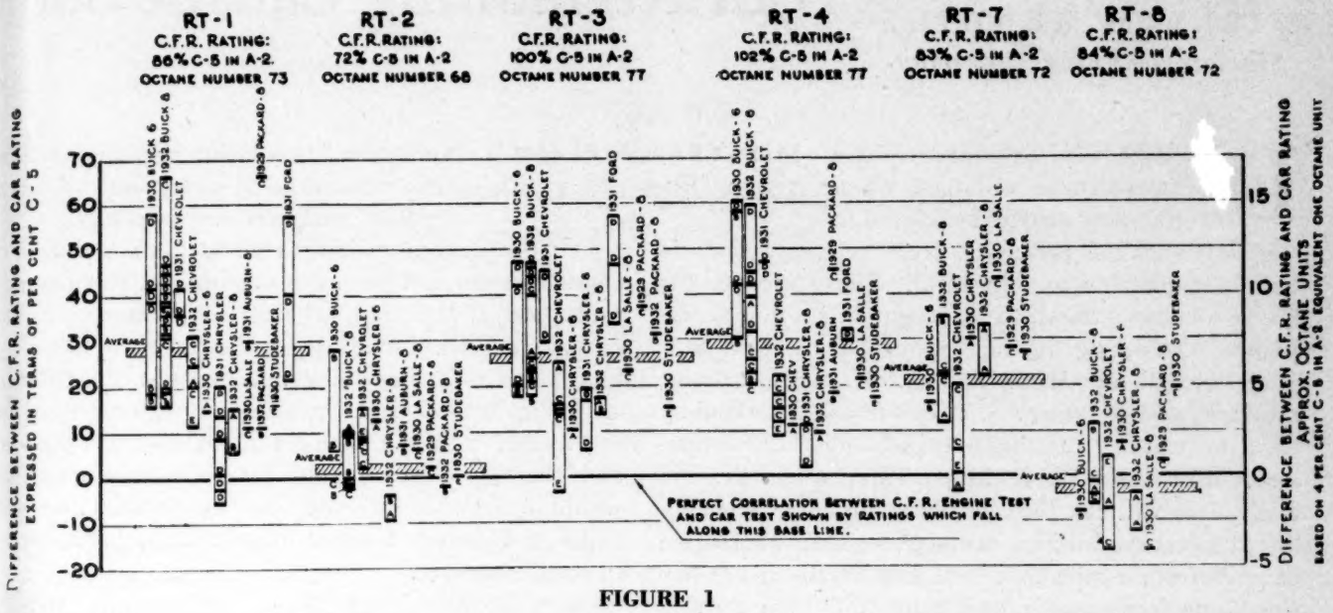



FIGURE 1

tory rating. It should be said also that some members of the sub-committee are experimenting with representative automobile engines, to see whether it is possible to modify them in such a way as to reduce the amount of the discrepancy that now exists between the ratings they give and those obtained by the present C. F. R. technique.

Only a general statement as to the results obtained in these studies on the C. F. R. apparatus and method can as yet be made; but it can be said that data thus far reported by the various investigators indicate that knock ratings on any given fuel or series of fuels which are in fair agreement with the behavior of the same fuels in any given car, or with the average behavior for a number of cars, can be obtained by suitable modifications of the C. F. R. apparatus and procedure, and obtained possibly all under the same uniform set of test conditions. The test conditions referred to cannot now be definitely specified, however, because there is not as yet available sufficient information: first, on just what rating should be obtained for some types of fuels; and, second, on just what test engine variables it will be most advantageous to modify. However, at its meeting, April 6, the sub-committee was of the opinion that no major changes in the C. F. R. unit will be necessary in order to correlate satisfactorily C. F. R. laboratory and road test results.

The point just mentioned is at once an important and an encouraging one, particularly from the viewpoints of those who now have C. F. R. knock-testing units in service and of those who may purchase them within the near future. At the time of the preparation of this report (April 12) there were in service 160 C. F. R. outfits. The majority of these were in the United States, but C. F. R. units were also in use in the following countries:

| | | |
|---|---|---|
| England | France | Germany |
| Poland | Russia | Italy |
| Egypt | South Africa | South America |
| Hungary | Australia | Czechoslovakia |

### CURRENT PROGRAM OF THE SUB-COMMITTEE

In the light of the above discussion, it is logical that the present work of the sub-committee should consist of the things on which it is now engaged, which are these:

1. To work out the best possible road test procedure, and then to rate typical present-day gasolines in representative cars by means of it.
2. To find means of getting knock ratings on the C. F. R. unit which will predict the behavior of fuels in cars; and as soon as the work on cars shall have shown just what the ratings of the various types of fuels in the laboratory ought to be, to settle upon the best possible setting of the different variables for the C. F. R. apparatus to give those ratings.

# *Preventing* Escape of Mercaptans In Reclaiming Caustic Soda

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MID-YEAR MEETING
TULSA, JUNE 1, 2, 3, 1932

DISPOSAL into the atmosphere of mercaptans obtained when reclaiming caustic soda used in washing gasoline recovered from refinery gases is both disagreeable and harmful. These mercaptans are in reality a mixture of organic sulphur compounds consisting of mercaptans, mecaptals, sulphides and di-sulphides of the $C_1$ to $C_3$ hydrocarbons, saturated and unsaturated. They are characterized by their powerful and lasting odor, which is very obnoxious. Although only relatively small quantities are evolved in the caustic reclaiming process, when allowed to escape into the atmosphere their odor often extends from a mile to a mile and a half on the leeward side from source, and hence they constitute a nuisance to the surrounding community. When exposed to small doses of these mercaptans no apparent harmful effect results, but with large doses headaches, nausea, and general ill-feeling results, which last over a period of days. Extreme sensitivity to additional exposure also results.

In reclaiming the caustic, the spent solution is preheated by means of heat exchange with the hot reclaimed solution and then introduced over the top tray of an atmospheric bubble tower. As this solution descends it is scrubbed of its mecaptans by means of heat application at bottom of tower and ascending stream or dry gas, or other suitable stripping agents. Heat is applied to the bottom of the tower by a closed steam coil, using approximately 100-pound steam, immersed in the hot caustic solution. This solution is maintained at the desired level by regulation of withdrawal through the heat exchanger, cooler, and thence to intermediate storage. The mercaptans and the stripping agents are removed from the top of tower as a vapor.

The means considered as substitutes for atmospheric disposal of such vapors were: solution or entrainment in water with sewer disposal, and combustion from a closed system.

As a first expedient, the vapor line was extended into an open sewer and the line well flushed with water. This practice lasted but a relatively short period due to the fact that complete solution in water did not take place or was not maintained so that atmospheric polution by mercaptans was concentrated at ground level around open sewer.

For the next step it was decided to maintain a closed system and burn the vapors in a flambeau at some part of the plant where open flames cause no hazard. As mentioned, dry gas or open steam may be used as stripping agents. When gas is used as a stripping agent a small amount of water should be introduced into the vapor line to cool the vapors and thereby condense out excess moisture which would otherwise drop out in the burner line and make continuous combustion difficult, particularly in cold weather.

The stripping gas should be substantially sulphur free, otherwise the caustic solution will be rendered useless for extended gasoline scrubbing due to accumulated formation of sodium sulphide. Sulphur free natural gas may be utilized; refinery gas must be scrubbed of its sulphur ($H_2S$ mainly) content. Since it was estimated that appreciable quantities of striping gas would be required, total gas from the stripper could be introduced into the plant gas fuel system. Both of these items involved operating costs and difficulties which were not considered warranted.

When open steam is used, a small stream of water has to be introduced into the vapor line to condense the steam. The condensed steam and water are trapped off and run into the sewer. Some of the mercaptans evidently go into solution with the water trapped out and, therefore, a tight connection to the sewer must be maintained. Otherwise, the mercaptan nuisance is evident in the immediate vicinity. This mercaptan bearing water is such an insignificant part of the plant sewer makeup that to date no ill-effects have been noted at the plant separators.

The vapors are led to a flambeau which is approximately 150 yards from the stripper. No difficulties have been encountered in delivery of these mercaptans to this flambeau. There are times when extraneous gas is required to maintain combustion, this gas being introduced into condensate trap at stripper. It is felt that the same effect may be had by the use of an extraneous gas fired torch at flambeau.

# Gas-Cracking *and* Reforming Processes

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***GASOLINE is the dominant product of the petroleum industry. Its manufacture is accompanied by large volumes of light hydrocarbon gases and vapors. There are several promising market outlets for these secondary products. Research, engineering, and sales development work have paved the way for commercial exploitation of these outlets. The technical problems pertaining to the utilization of these light hydrocarbon gases and vapors have for the greater part been solved. Rapid strides have been made in marketing liquefied petroleum gases. The supply of motor fuel and commercial gases can be increased by appropriate gas-cracking and reforming processes recently developed. These developments make it possible to enlarge the markets for these light hydrocarbon vapors and gases. The main problem that now confronts the industry is an appreciation of the necessity for cooperative and economic cultivation of the markets which are now awaiting further exploitation.***

MID-YEAR MEETING
TULSA, JUNE 1, 2, 3, 1932

THE petroleum industry, engaged as it is in the manufacture of finished products from raw materials, has during any particular period of its development been governed largely by the demand for one dominant commodity. Prior to about 1900 the dominant product was kerosene, and subsequent to that time gasoline has played the major role, with lubricants of secondary importance.

The manufacture of the dominant commodity is controlled by the law of supply and demand, and the volume in most instances governs the amount of secondary products. During the initial development of any industry, in which the profits are high and ample raw material is available, little or no attention is paid to the possibilities of incidental or secondary products. In fact, they are often considered as necessary waste. Increasing competition, resulting in a small margin of profit, makes the necessity of utilizing secondary products one of great economic importance. Leaders of the oil industry have foreseen the end of this initial period of easy profits and the necessity for creating and developing new markets for petroleum products. The general economic conditions of recent years have emphasized this viewpoint.

The decision to proceed on a program of creating and expanding markets should be based upon a complete and unbiased survey of the present and probable future demand for the proposed products and upon the effect of their increased supply on other industries which are now furnishing the same or similar commodities.

The primary function of the petroleum industry is to supply fuel and lubricants, the disposal of incidental products being of secondary importance. In the past the rapid growth of the automobile industry has taxed the ability of the petroleum industry to provide motor fuel. It is only natural under these conditions that the major effort should be directed toward the manufacture and distribution of gasoline with other outlets receiving little attention. Recent economic conditions, within and outside the industry, have combined to make it necessary seriously to consider other promising markets. A study of the present and potential markets reveals the following possibilities:

1. Direct utilization of lequefied petroleum gases, by which they are used without further processing in the gas-manufacturing, industrial-gas, and domestic-gas fields.
2. Motor fuel markets and gas industry outlets. Vapors and gases can be cracked with the simultaneous production of motor fuel for the gasoline trade and a gas for use by the gas industry.
3. Use of gas-reforming processes by the gas industries:
   a. Reforming hydrocarbons by passage through incandescent fuel bed in water-gas plants.
   b. Continuous process for producing reformed gas of comparatively high thermal value.
   c. Continuous process which may be used to produce a gas which will duplicate gravity and heating value of natural gas or present manufactured gases.
4. Markets in the chemical industries.

This paper is confined to a brief discussion of the economic importance of the above-mentioned markets

and the ways and means by which they are being developed.

## DIRECT UTILIZATION OF LIQUEFIED GASES

The gas industry and the industrial and domestic fuel markets are important outlets for petroleum products. The coal industry provides about 60 per cent of the fuel requirements of the United States. The percentage supplied by the petroleum industry is only about half of the amount attributed to the coal industry, but the percentage contributed by petroleum products has doubled during the past decade. However, it is evident that there still remains a large potential outlet for liquid and gaseous fuels without incurring serious inter-commodity competition within the petroleum industry.

The use of liquefied petroleum gases, such as propane and butane, has steadily increased from 1.1 million gallons in 1927 to 28.5 million gallons in 1931. The estimated potential supply of these products by the natural gasoline industry alone is 13 million gallons daily. Since the investment in equipment and the major expense of producing a portion of the potential production are incidental to the manufacture of natural gasoline and motor fuel, the petroleum industry is justified in going to considerable expense and effort to create and develop markets for these gases. Marketers entering the field seem to fail to recognize that the main problem is to originate new markets in an unsaturated field. In most cases they resort to price cutting and other uneconomic practices prevailing in those businesses whose markets are practically saturated. It certainly would be to the best interest of all—and this applies to the producers of manufactured gas as well as it does to liquefied petroleum gas manufacturers—if the money lost by price cutting were used for research, engineering, and sales purposes in order to create and develop new markets instead of donating it to the old customers who are already sold on the advantages of gas.

Pronane is rapidly becoming an important domestic fuel. The greatest portion of the progress made in finding markets for propane has been in suburban districts not supplied with natural or manufactured gas. This product comprises the bulk of the so-called "bottled gases." A large investment is required to exploit this business. Consequently, the importance of the investment overshadows the value of the fuel outlet.

The use of butane for enrichment of manufactured gas, to meet peak loads and to increase the capacity of gas-manufacturing equipment, has been rapidly extended during the last five years.

The butane-air system has made it possible to distribute gas in communities which are not large enough to support other established gas-making processes. The above-mentioned uses for liquefied petroleum gases have not by any means reached the saturation point. However, the physical properties of these gases (such as specific gravity and dew points) have set up limitations which in some specific instances narrow their fields of application. A number of gas-cracking and reforming processes have been proposed to overcome such limitations and thereby provide an even broader scope of utilization than is enjoyed at present.

## MOTOR FUEL MARKETS AND GAS INDUSTRY OUTLETS

The demand for increase in quantity and for improvement in quality of motor fuel has brought about several economic changes in the petroleum industry. One of these changes has been the increased production and the conservation of the lighter hydrocarbon vapors and gases.

Due to the many assumptions that must be made, any estimate of the quantity of hydrocarbon vapors produced by the petroleum industry is open to criticism. A recent estimation indicates that 349 million cubic feet of refinery vapors are produced per day by 62 major refineries in the United States east of the Rocky Mountains. In addition to this, there is immediately available for the natural gasoline industry a supply of 750,000 gallons daily of liquefied petroleum gas which will eventually find markets at competitive prices. These vapors and gases constitute a raw-material loss which represents a large item of the final manufacturing cost of motor fuel. This situation has been responsible for the wide-spread and growing interest shown by refiners and natural gasoline manufacturers in the methods and equipment necessary for producing motor fuel from hydrocarbon vapors and gases. The geographical location, as well as the quantity and quality of this supply of these hydrocarbon vapors, places certain controlling limits on their proposed uses. An ideal market would be one which is capable of economic absorption of any future increase in their production. Gas-cracking processes capable of producing motor fuel having a high benzol content give promise of meeting this ideal situation, and in addition assist in filling the increasing demany for a gasoline of high anti-knock value.

The equipment necessary for cracking hydrocarbon vapors to produce motor benzol (light oils) consists of a tube-type of furnace, a reaction chamber, and a benzol-light-oil-recovery system, with the necessary accessories such as pumps, recording instruments, etc. The hydrocarbon vapors to be cracked are heated to 1300°F. to 1400°F. in the tubes. During this heating period endothermic reactions take place which result in the formation of the maximum concentration of unsaturated hydrocarbon gases. The hot gases from the coils enter the insulated reaction chamber where the exothermic reactions take place, during which the benzol-light oils are formed. These exothermic reactions may cause the temperature of the gases within the reaction chamber to rise 100°F. or more. The hot gases leaving the reaction chamber have a sensible heat content of approximately 85,000 B.t.u. per 1000 cubic feet. If the process is operated in connection with a refinery, this sensible

heat can be used to pre-heat the charge going to the cracking stills, to top or pre-heat crude oil, or to crack oil by direct contact in the vapor phase. In most operations made in conjunction with the refinery, the benzol and other light oils produced by gas cracking will be mixed with the other refinery vapors. In such cases the benzol-light oils will be recovered with the gasoline products, and no additional light-oil-recovery equipment will be necessary.

The gas resulting from the pyrolysis of hydrocarbon vapors and gases to produce motor fuel is in certain respects more useful to the gas industry than are the original hydrocarbon vapors. By means of a slight sacrifice in benzol-light-oil yield, a rather wide range in quantity and quality of the gas can be obtained. Gases ranging from approximately 0.45 to 0.75 specific gravity and from about 875 to 1300 B.t.u. have been produced in commercial-size plant operation. Operating conditions can, therefore, be adjusted to take full advantage of the relative economics of the two concomitant products. This favorable situation, as well as the flexibility of producing a gas whose properties can be varied through wide ranges, enlarges the field of utilization of the light hydrocarbon vapors.

The cracking of gases to produce motor benzol generally results in a volume increase of more than 100 per cent with an over-all B.t.u. reduction of less than 25 per cent. The increase in hydrogen content of the cracked gas suggests a number of interesting uses in connection with refinery operations. The low-boiling fractions of the benzol-light oil and the unsaturated-hydrocarbon content of the cracked gas, which are subject to the control of the process, represents a source of raw material for an extensive chemical industry.

## USE OF GAS-REFORMING PROCESSES BY THE GAS INDUSTRIES

### *a. Reforming Hydrocarbons by Passage Through Incandescent Fuel Bed in Water Gas Plants*

The reforming of hydrocarbon vapors has been applied to existing manufactured gas processes in various ways. Petroleum products, such as butane, are passed through an incandescent fuel bed in the blue water-gas equipment. The decomposition of the butane is accompanied by the formation of saturated and unsaturated hydrocarbons, hydrogen, and carbon—the relative proportions of these substances depending upon operating conditions. The heating value of the resulting gas mixture is controlled by varying the rate of butane throughput and by other changes in operating conditions. This reforming process increases the capacity of the water-gas equipment and is, therefore, a distinct advantage in meeting peak-load requirements by increasing the output of the existing gas-manufacturing installations. Its disadvantage resides in its dependence upon the use of high investment in water-gas equipment and the decrease in thermal efficiency of hydrocarbon utilization.

### *b. Continuous Process for Producing Reformed Gas of Comparatively High Thermal Value*

In some instances it is advantageous to the gas industry to have gas available which has a comparatively high B.t.u. content and which is not dependent upon already-installed gas-manufacturing equipment. In such cases, peak-load requirements, seasonal maximum-load demand and/or a standby process to insure uninterrupted service are the principal features to be considered. To meet these conditions the gas-reforming process must possess a low installation investment, the raw material must be abundant, the storage cost for raw material must be low, the raw material must not deteriorate in storage, and the equipment must be so designed that the process can be put in operation on short notice. To supply this need a continuous hydrocarbon vapor-reforming process has been developed that is continuous in operation and independent of all other gas-manufacturing equipment. The thermal value and specific gravity can be controlled during processing to produce a gas that can be mixed with water gas, manufactured gas or natural gas to adjust its B.t.u. value as desired. This process can be used independently of other processes to supply a gas uniform in gravity and heating value where a gas of high B.t.u. content is desired. A hydrocarbon, such as butane, can be reformed to any desired B.t.u. value between 1700 and 3200 with a corresponding change in specific gravity. The predominating chemical reactions taking place during the reforming period are endothermic. A plant producing 8000 cubic feet of 1700 B.t.u. gas per hour has been operated for 135 days without any trouble with carbon formation in the heating coil. All indications are that the process can be operated indefinitely without appreciable difficulty in this connection.

The reforming equipment consists of a tube-type of furnace of any proven design equipped with coils of heat-resisting alloy. The apparatus is similar to that described above in the manufacture of benzol-light oils. No catalyst or reaction chamber is necessary. The tubes and furnace must be designed to provide for the proper capacity and rate of heat input. The temperature of the reformed vapor at the exit of the furnace should be from 1000°F. to 1400°F., depending upon the type of gas desired. Tubes of 18-8 nickel-chromium alloy have been used successfully under these operating conditions. In a properly designed furnace the maintenance cost of alloy tubes is not prohibitive. Operation and control of the process to produce a gas of constant calorific value are simple. Inexperienced labor has operated this process with not more than one per cent variation in the B.t.u. value of the gas produced over a period of one week. This exactness of control of gas quality was accomplished without the use of a gas-holder.

The concentration of hydrogen and unsaturated hydrocarbons in the reformed vapor increases as the re-

forming reactions progress. The unsaturated hydrocarbons reach a maximum concentration of 43 to 48 per cent when butane is reformed to 1700 B.t.u. value. A typical analysis of such a product is shown in Table 1. A series of analyses taken during the reforming period show that the concentration of the individual unsaturated hydrocarbons changes as the reforming progresses. If the reforming process is to be used as a source of unsaturated hydrocarbons for the manufacture of chemical products, the reforming conditions can be controlled so as to obtain the maximum yield of the desired unsaturated hydrocarbon.

**TABLE 1**
**Analysis of Reformed Butane**

| | (Per Cent by Volume) |
|---|---|
| Hydrogen | 9.9 |
| Methane | 22.8 |
| Ethane | 4.2 |
| Ethylene | 25.2 |
| Propylene | 16.8 |
| Butylene | 4.4 |
| Butane and heavier | 16.7 |
| Specific gravity | 1.0 |
| B.t.u. value | 1,700 |

*c. Continuous Process Which May Be Used to Produce a Gas Which Will Duplicate Gravity and Heating Value of Natural Gas or Present Manufactured Gases*

In addition to the desirable features of the process just described, the ideal gas-reforming process should also be sufficiently flexible to produce a gas with a B.t.u. value and specific gravity corresponding to natural gas or to any of the existing manufactured gases. A gas process of this latter type would afford a direct substitute for natural gas and for manufactured gases; and, therefore, has a much wider field of application in the gas industry. In addition, there has been a long-felt need for a process that would make it possible to reduce investment costs per unit volume of gas delivered through high-pressure transmission lines. For example, in order to supply natural gas to the ultimate consumer at as low a price as possible, and at the same time obtain the most satisfactory return on the investment, it is necessary to operate a natural-gas pipe line at the highest possible percentage of its capacity. The demand for gas generally increases during the fall of the year, reaching a maximum in January or February with a corresponding decrease in the spring of the year. In some instances the peak demand for domestic fuel during the winter has been 400 per cent of the average summer demand. This situation will tend to become more serious as the space-heating load becomes more fully developed.

The natural-gas pipe line companies have attempted to compensate for low-load factors of their lines by selling gas to the consumer on a sliding scale by seasonal price changes and by low off-peak load prices. Such devices distribute the burden between the pipe line companies and the consumer, but do not fully remedy the situation. A more satisfactory solution is to supplement the natural gas supply during the peak-load periods by a gas-manufacturing process which will duplicate the B.t.u. and specific gravity of the natural gas. A manufactured gas of this type can be mixed with natural gas in any desired proportion without materially changing the practical combustion characteristics of the natural gas. With the above-mentioned combination of conditions in mind, a new gas-manufacturing process has been developed.

The equipment necessary for this process is a tube-furnace with alloy heating coil similar to the gas-reforming equipment described immediately above. No additional equipment, such as a reaction chamber, is necessary. The process is continuous, and is based on the combination of hydrocarbon-reforming and water-gas reactions. The combination of reactions is carried out simultaneously, and can be controlled to produce gas with a range of B.t.u. and specific-gravity values wide enough to enable one to duplicate those properties of any of the existing natural or manufactured gases. A mixture of steam and hydrocarbon is passed through the heated coil containing a catalyst. By the proper control of the steam to hydrocarbon-ratio, the temperature, time of contact, and rate of heat, input-gases ranging from 260 to 1800 B.t.u. can be produced. The process can be successfully operated, using petroleum products embodied in the range of natural-gas hydrocarbons, thereby insuring an abundance of raw materials which is an additional factor in broadening the fields of application. The results shown in Table 2 were obtained with the use of commercial butane as the raw material. Utility companies which distribute a mixture of natural gas and manufactured gas of low B.t.u. value, such as blue water gas, can increase their natural gas-load factor during the summer months by using natural gas as a raw material in this new gas-manufacturing process.

**TABLE 2**
**Analysis of Gases Made by New Process Showing Its Adaptability for Duplicating Qualities of Other Commercial Gases**

| | | | | | |
|---|---|---|---|---|---|
| Specific gravity | 0.45 | 0.52 | 0.55 | 0.62 | 0.86 |
| B.t.u. value (gross) | 453 | 609 | 666 | 809 | 1,266 |
| Carbon dioxide | 7.2 | 3.6 | 6.4 | 5.0 | 4.6 |
| Carbon monoxide | 18.2 | 13.3 | 15.0 | 15.0 | 10.4 |
| Hydrogen | 55.4 | 47.7 | 44.9 | 43.6 | 38.1 |
| Unsaturated hydrocarbons | 4.3 | 8.3 | 9.5 | 12.9 | 13.3 |
| Paraffin hydrocarbons | 14.9 | 27.1 | 24.2 | 23.5 | 33.6 |

**MARKETS IN THE CHEMICAL INDUSTRY**

The extension of the art of fractionation in the petroleum industry has made large quantities of relatively pure hydrocarbons of the paraffin series available for manufacturing chemicals. The extensive use of crack-

ing processes, the development of vapor-reforming processes, and the development of processes to produce unsaturated and aromatic hydrocarbons have increased the supply of raw materials for many chemical products. Although this outlet for hydrocarbon products is extensive in regard to the number of chemical compounds that can be manufactured, the actual quantities of the various hydrocarbon products which can be economically used are small in comparison with the supply.

One of the largest outlets so far developed for hydrocarbons in the chemical industry has been the production of carbon black. The channel process using natural gas continues to produce the major portion of the carbon black used. This process is repeatedly accused of wasting natural resources. Natural gas conservation measures are becoming more restrictive, and the problem of an adequate supply of natural gas for carbon black may before long become a serious one if the quantity of natural gas profitably distributed by pipe lines continues to increase. In the past it has been necessary for the carbon black industry to locate its plants in the field where the natural gas is produced. The development of gas-cracking and vapor-reforming processes will have a marked effect on this situation. Actual experimental results have shown that a very satisfactory carbon black can be made by using butane in the channel process. It has also been found that the actual quantity of carbon black produced per unit volume of hydrocarbon vapors can be increased by reforming the vapors prior to their use in the channel process. It has also been shown that a heavy hydrocarbon vapor, such as buntane, can be cracked to produce concurrently benzol-light oils and a resulting gas—which after extracting the benzol—can be used to manufacture carbon black giving a yield equal to that capable of being produced from the original vapors. The results of these investigations reveal that the future of the carbon black industry is not dependent upon the abundant supply of natural gas, and that any prohibitive legislation in regard to natural gas need not limit carbon black production.

Benzol will continue to find its major outlet in the motor fuel field. However, the quantity of benzol used in the chemical industry is large and growing. The nation's supply of benzol and toluol during war is highly important. The development of a process to produce these compounds from petroleum assures an ample supply in case of a national emergency.

In general, the demand for special petroleum products by the chemical industry will affect individual companies more than the industry as a whole. Certain individual companies will find themselves in a position advantageously to supply certain products. It is important that these individual companies fully recognize this situation, and develop markets for special products accordingly.

# The Decreasing Export Markets

As the American refining industry looks into the future a continued decrease in its export markets is seen. Development of refining in most of the foreign countries formerly important customers of the industry in this country is rapidly assuming more threatening proportions.

Russia and Canada are perhaps more aggressive in the formation of refining industries than others, and of the two, Russia has quickly become an important competitive factor abroad. Canada, although thought to be expanding its refineries to take care of home consumption, will no doubt export more refining products to its mother country, England.

Canada, during the past year has added five refineries to its active list. Recently two major companies operating in the United States announced plans for immediate construction of plants there. This country, through its import duties and anti-dumping laws continues to offer serviceable protection to its growing refining industry, and at the same time forcing American companies operating there to establish refineries. Ultimately Canada will develop its producing fields to the point where much less crude oil will be received within its borders.

France is protecting its petroleum refining industry, erecting four refineries, but erection in France is necessarily slow because of restrictions as to manufacture and source of equipment. Germany and Italy likewise impose restrictions as to manufacture, but are forging ahead in the establishment of their own refining industries. Expansion continues in England, but to a lesser degree.

Continental Europe and Canada are being removed as export markets. The American industry is confronted with a slowly increasing domestic demand for its products, and a rapidly decreasing export market. Perhaps the answer is new research, new products, new fields—and less over expansion of refining capacity.

# DESIGN CALCULATIONS *for* Vapor Recovery and Rectifying Units

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*BECAUSE of its importance to the industry, distillation of petroleum products has been a popular field of investigation. Many formulas and methods for computing the number of plates, and proportions of the column have been proposed from time to time. Some of these methods have found practical application in particular cases, but none of them has been found adequate as a basis for accurate design calculations for equipment operating over a pressure range up to 500 pounds per square inch.*

*Methods of design based upon the separation of two components are obviously inadequate when treating a complex mixture such as refinery gas, or absorption gasoline, particularly when efficient operation demands that the equipment recover all of the material of greater molecular weight than butane while making a sharp separation in the butanes to meet modern vapor pressure limitations without excessive losses.*

*The universal assumption of the validity of Raoult's and Dalton's Laws as applied to hydrocarbon mixtures is a serious limitation, particularly when operating at pressures greater than atmospheric.*

*The procedure outlined in this paper has been found sufficiently accurate for engineering computations and otherwise entirely satisfactory for the design of absorption and rectifying equipment for gasoline when operating at pressures up to 500 pounds per square inch. Although still far from perfect it is a convenient and accurate method which is considered a distinct improvement.*

*The use of Raoult's Law in the design of gasoline absorbers indicated that about four times as many plates were required at 500 pounds pressure as would be expected from the available operating data at 40 pounds pressure. Such large errors have been eliminated by avoiding the assumption of Raoult's Law. Actual equilibrium conditions have been more closely approximated by the assumption of ideal solutions which is substantially accurate under these operating conditions except for the solubility of gases such as methane in material of high molecular weight such as absorption oil. At least plates of the same design are found to have the same efficiency at 40 or 400 pounds pressure instead of a loss in efficiency from 40 per cent at 40 pounds to about 10 per cent at 400 pounds as is indicated by Raoult's Law.*

MID-YEAR MEETING
TULSA, JUNE 1, 2, 3, 1932

## PRESSURE-VOLUME TEMPERATURE RELATIONS OF PARAFFIN HYDROCARBONS

In order to compute the deviations from the ideal gas laws, and to determine the equilibrium between gaseous and liquid hydrocarbons by the assumption of ideal solutions, it was necessary to develop a reduced equation of state for the paraffin hydrocarbons.[1]

Figure 1 shows the deviation from the ideal gas laws for the paraffin hydrocarbons up through pentane plotted as a function of reduced pressure as lines of constant reduced temperature. The reduced pressure is determined by dividing the total absolute pressure by the critical pressure. Similarly the reduced temperature is determined by dividing the absolute temperature by the absolute critical temperature of the particular compound under consideration.

Although the chart does not include compounds of molecular weights greater than pentane, the pentane lines may be used for the higher molecular weight compounds with a fair degree of precision.

The development of this chart is fully described in the original reference and it is included here because of its use in making design calculations. Table I gives the critical constants for the paraffin hydrocarbons through normal octane which may be used in determining the deviations from the ideal gas law for these compounds in conjunction with the chart shown in Figure 1. The compressibility factor (z) as plotted in Figure 1 is a direct indication of the deviation from the ideal gas law, since the product z R T equals P V. Under many conditions the departure from an ideal gas is so large

[1] Brown, Souders and Smith—Ind. Eng. Chem. 24, p. 513, May, 1932.

**TABLE 1**
**Critical Constants for Paraffin Hydrocarbons**

| Hydrocarbon | Critical Temp. | | Critical Pressure | | Critical Vol. | | Reference |
|---|---|---|---|---|---|---|---|
| | °R | °K | Lb./sq. in. abs. | Atms. | Cu. ft./lb. mole | Cc./g.mole | |
| Methane | 344 | 191 | 673 | 45.8 | 1.59 | 99.3 | Intern. Critical Tables |
| Ethane | 550 | 305 | 709 | 48.2 | 2.19 | 136 | Intern. Critical Tables |
| Propane | 664 | 369 | 632 | 43.0 | 3.04*a* | 190*a* | Intern. Critical Tables |
| Isobutane | 733 | 407 | 544 | 37.0 | 4.00*a* | 250*a* | Intern. Critical Tables |
| *n*-Butane | 767 | 426 | 529 | 36.0 | 4.00*a* | 250*a* | Intern. Critical Tables |
| Isopentane | 830 | 461 | 484 | 32.9 | 4.85 | 303 | (9) |
| *n*-Pentane | 847 | 470 | 485 | 33.0 | 4.97 | 310 | (9) |
| Diisopropyl | 901 | 501 | 452 | 30.7 | 5.72 | 357 | (9) |
| *n*-Hexane | 914 | 508 | 435 | 29.6 | 5.88 | 367 | (9) |
| *n*-Heptane | 972 | 540 | 396 | 27.0 | 6.85 | 428 | (9) |
| Diisobutyl | 990 | 550 | 361 | 24.5 | 7.73 | 482 | (9) |
| *n*-Octane | 1025 | 569 | 362 | 24.6 | 7.86 | 490 | (9) |

*a* Interpolated values.

that this deviation may not be overlooked without serious error.

## EQUILIBRIA BETWEEN LIQUID AND VAPOR SOLUTIONS OF PARAFFIN HYDROCARBONS

The conventional use of Raoult's and Dalton's Laws leads to the equation

$$Py = px$$

where P = total pressure
y = mol fraction of individual component in the gas phase
p = vapor pressure of component in the liquid phase
x = mol fraction of component in liquid phase

From this equation

$$\frac{y}{x} = \frac{p}{P}$$

is this ratio $\frac{y}{x}$ which determines the change in composition between vapor and liquid. This ratio is defined as K in the following chart.

If the gaseous and liquid solutions are considered as ideal,

$$\frac{y}{x} = K = \frac{f_L}{fV}$$

where $f_L$ = fugacity of pure liquid at the same temperature and total pressure

$fV$ = fugacity of pure vapor at the same temperature and total pressure.

The fugacities of the liquid and vapor hydrocarbons have been computed[2] from the pressure volume temperature relations as indicated in Figure 1.

The values for these equilibrium constants are plotted in Figure 2 as a function of total pressure as lines of constant reduced temperature for the low molecular weight paraffin hydrocarbons.

This plot may also be used for estimating the values of K for the higher molecular weight components by determining the vapor pressure of the pure component at the desired temperature thereby locating the total pressure at which the value of the equilibrium constant $\left(K = \frac{y}{x}\right)$ has a value of unity. The desired value for K at any total pressure at the chosen temperature may then be estimated by continuing a line through this point parallel to the pentane line of the same reduced temperature and reading the intersection of this line with

[2] Ind. Eng. Chem. 24, p. 515, May 1932.

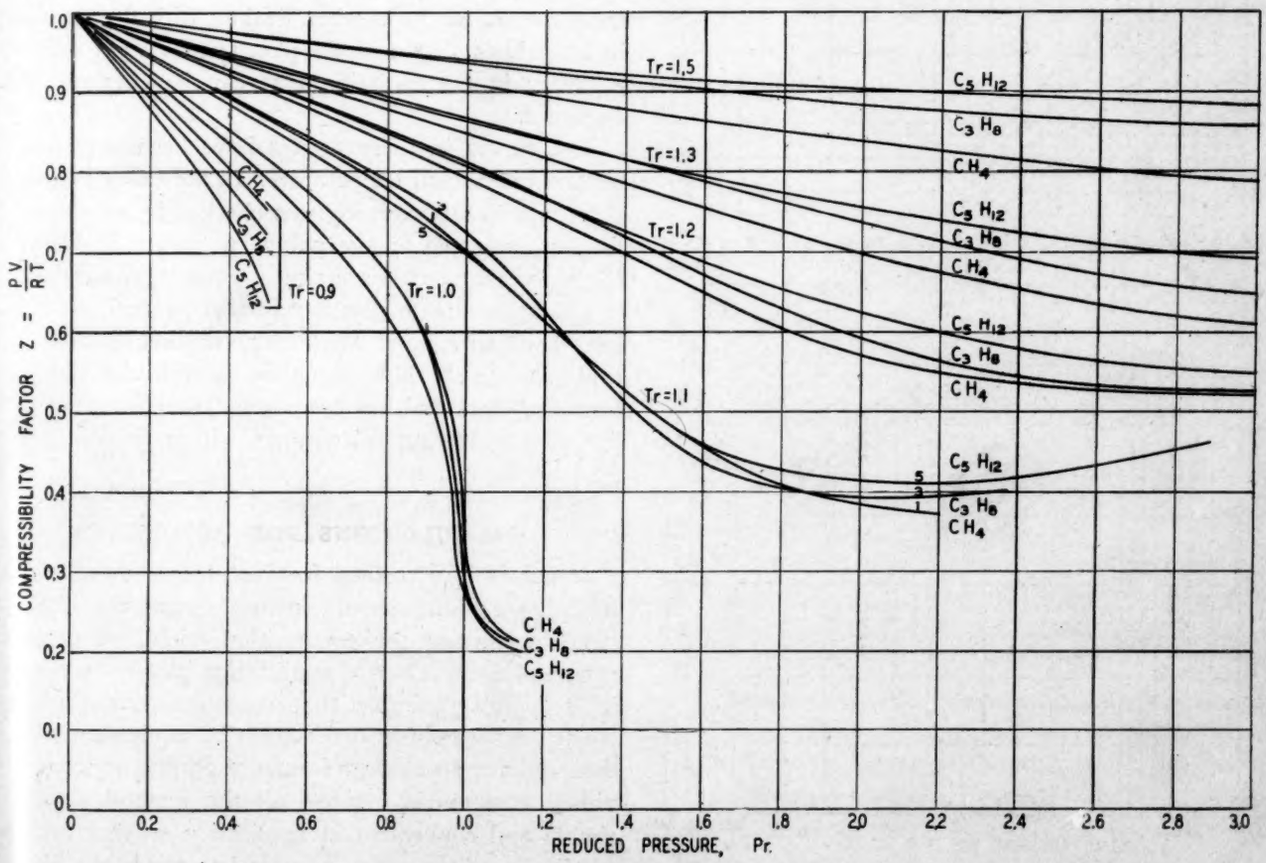



**FIGURE 1**
***Deviations from the Law of Ideal Gases.***

the ordinate of the desired total pressure. For example find the equilibrium constant, K, for n-heptane at 220°F. and 100 pounds per square inch absolute total pressure.

At 220°F. the normal vapor pressure of heptane is 17.4 pounds per square inch, therefore the K for heptane at 220°F. is equal to unity at 17.4 pounds per square inch. Since 220°F. corresponds to a reduced temperature of 0.7 for n-heptane, a curve passing through K = 1 and P = 17.4 may be constructed parallel to the curve for 0.7 reduced temperature for n-pentane on Figure 2. From this curve at 100 pounds per square inch, the value of K for n-heptane at 220°F. is found to be 0.23.

Similar curves developed for other reduced temperatures may be used to determine a series of points at constant pressure which serve to construct for heptane a curve of K as a function of temperature similar to Figures 3, 4 and 5, with results as tabulated in Table 2.

These extrapolated values for the higher molecular weight compounds are less accurate than those for the hydrocarbons indicated in Figure 2 not only because of the extrapolation but also because the mixture of high and low molecular weight hydrocarbons seem to depart appreciably from ideal solutions. This deviation from ideal solutions will not introduce appreciable error in any engineering calculations when mixtures of methane through pentane are considered, or when mixtures of ethane through octane are considered.

[3] Ind. Eng. Chem. 23, p. 548, May 1931.

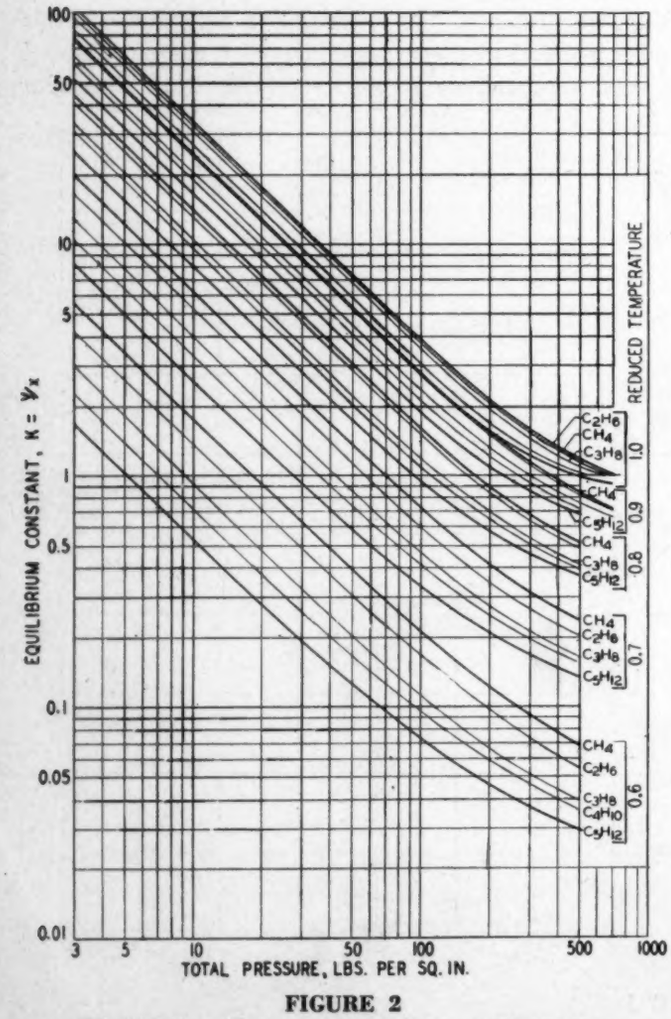



**FIGURE 2**

***Equilibrium Constant as Function of Pressure.***

**TABLE 2**

**K for n-heptane at 100 pounds per square inch absolute**

| Reduced Temperature | Temp. | K |
|---|---|---|
| Tr | °F. | |
| 0.6 | 123 | 0.053 |
| 0.7 | 220 | 0.23 |
| 0.8 | 317.6 | 0.73 |
| 0.9 | 415 | 1.5 |
| 1.0 | 512 | 2.5 |

Methane shows a noticeable deviation from an ideal solution when dissolved in the heavier hydrocarbons. In the case of an absorption oil with a molecular weight of about 160 correct results are obtained if the methane is assumed to have a value for the equilibrium constant about twice that indicated for an ideal solution. This apparent deviation from ideal solutions of methane may be larger than actual because of smaller but yet appreciable deviations of ethane. Frolich, Tauch, Hogan and Peer[3] have also indicated a deviation from the ideal solution of about this order of magnitude for methane dissolved in heavy naphtha or gas oil.

In Figures 3, 4 and 5 the values for the equilibrium constants of the paraffin hydrocarbons from methane through normal pentane are plotted as a function of temperature for constant pressure of 100, 200, 300, 400 and 500 pounds per square inch absolute. This is the most convenient form when dealing with the particular hydrocarbons shown in the plot, but does not offer the accuracy in extrapolation that can be obtained from Figure 2.

The curves in these figures have been extrapolated beyond the critical temperature. In the case of methane these extrapolations have been checked by experimental data as indicated by the points in Figure 3. Data for the other compounds are almost entirely lacking.

The approximate accuracy of these values for K has been checked against equilibrium vaporizations of natural gasoline and light naphthas, as well as actual plant operating data and has been found sufficiently accurate for all engineering calculations within the range covered by the chart.

## CALCULATIONS FOR ABSORBERS

A satisfactory method for calculating absorbing and stripping columns should include means for quantitatively evaluating the composition, yield, oil or steam rate, and the number of equilibrium plates. In addition it is highly desirable that each component may be treated separately in order that the equipment may be designed for specific performance on one or more individual compounds. Above all the method should be simple and convenient in application so that optimum conditions of operation may be determined readily.

The following method is an extension of the work

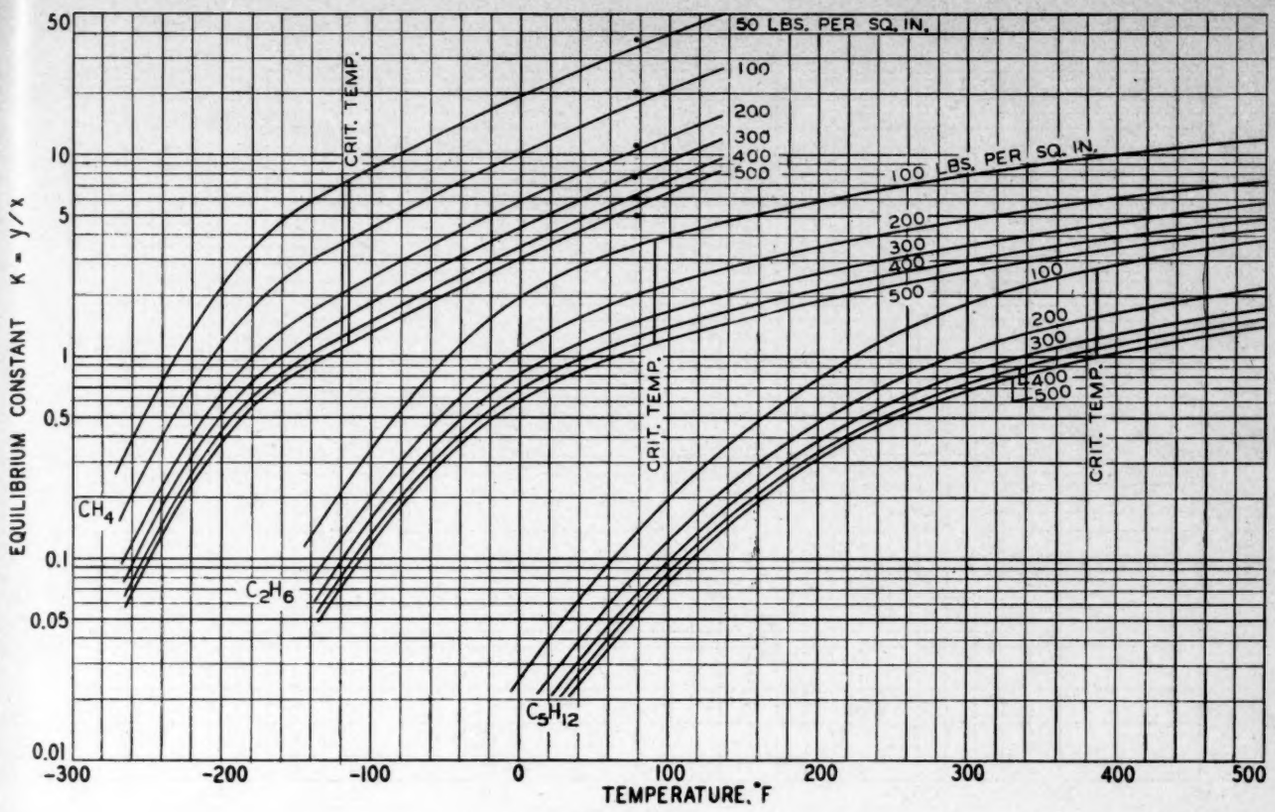



**FIGURE 3**

***Equilibrium Constant as Function of Temperature***

of Kremser and has been found satisfactory and convenient in application.

In the derivation of the equations it was assumed that the temperature, pressure and quantities of gas and oil are constant throughout the column. But in actual application satisfactory results may be obtained when these conditions are not fulfilled by determining an average affective temperature or oil rate for the entire column.

It is not necessary to assume Raoult's Law or the ideal gas laws. The value for the equilibrium constant, and the deviation from the ideal gas laws as indicated in this paper may be used to obtain satisfactory results.

The following equation

$$\frac{y_{n+1}-y_1}{y_{n+1}-y_0}=\frac{A^{n+1}-A}{A^{n+1}-1}$$

in which

$y_{n+1}-y_1$ = Actual change in composition of the gas

$y_{n+1}-y_0$ = Maximum change in composition of the gas that would be brought about if the gas leaving the top of the absorber were in equilibrium with the lean oil, or if there were an infinite number of plates.

L = Total mols of liquid

V = Total mols of gas

x = Mol fraction of a component in the liquid

y = Mol fraction of a component in the gas

$K=\frac{y}{x}$ = Equilibrium constant—a function of temperature and total pressure for each component.

n = Number of plates, starting at top plate of absorber; when used as a subscript indicating the plate of origin from which the liquid overflows or the vapor rises.

M = Molecular weight of absorbent oil

d = Specific gravity of absorbent oil (at 60°F.)

G = Gal. oil circulated per 1000 standard cu. ft. of gas (measured at 60°F. and 14.7 lbs. per sq. in. absolute).

A = Absorption factor for each component $=\frac{L}{KV}=\frac{3.156\ dG}{KM}$

represents the operation of an absorber and has been completely derived elsewhere.[4] The equation includes all the important variables in the absorption of any one component and may therefore be applied to any single component, or in turn to all of the components in the mixture.

The graphical solution of this equation is given in Figure 6 which greatly simplifies the calculations for the solution of this equation.

In determining the absorption factor, the oil-gas ratio at the bottom of the column is used, and the mean effective temperature is determined as the weighted mean temperature throughout the column.

Low pressure absorbers operating on lean gases closely approximate constant oil gas rates and constant temperatures throughout the absorber. For this reason it is usually more convenient to take the oil and gas quantities as entering the absorber for determining the oil rate and to use the temperature of the oil as the mean effective temperature of the absorber. The latter as-

[4] Souders and Brown, Ind. Eng. Chem. 24, p. 519, May 1932.

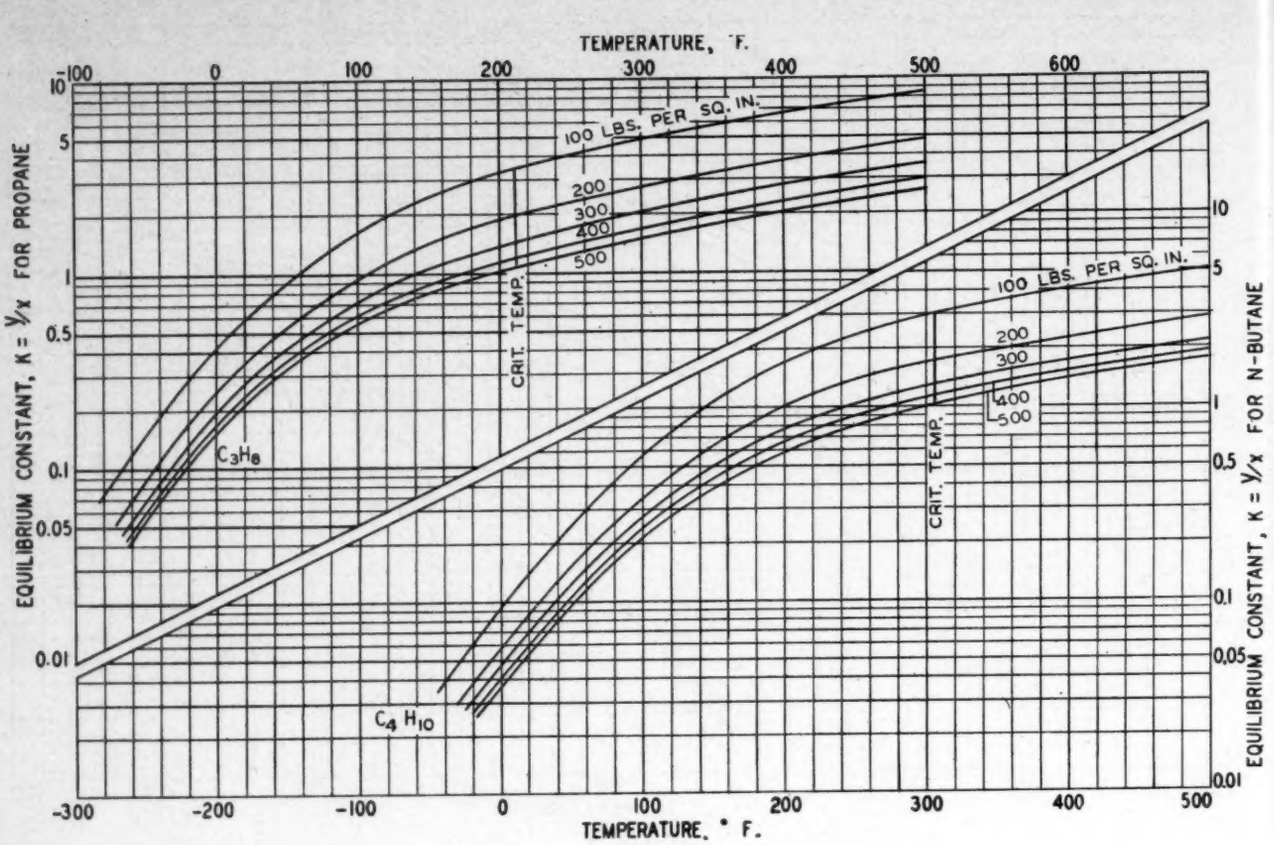



**FIGURE 4**
***Equilibrium Constant as Function of Temperature.***

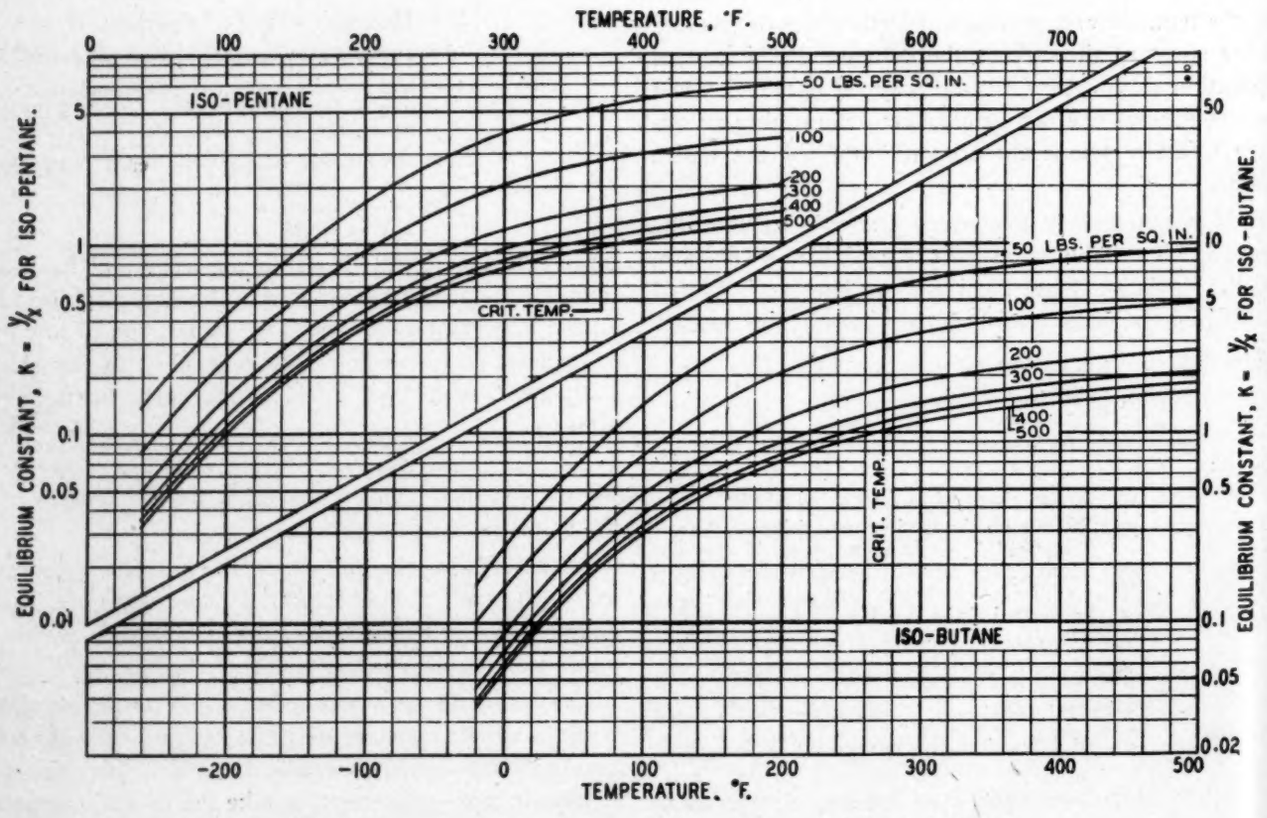



**FIGURE 5**
***Equilibrium Constant as Function of Temperature.***

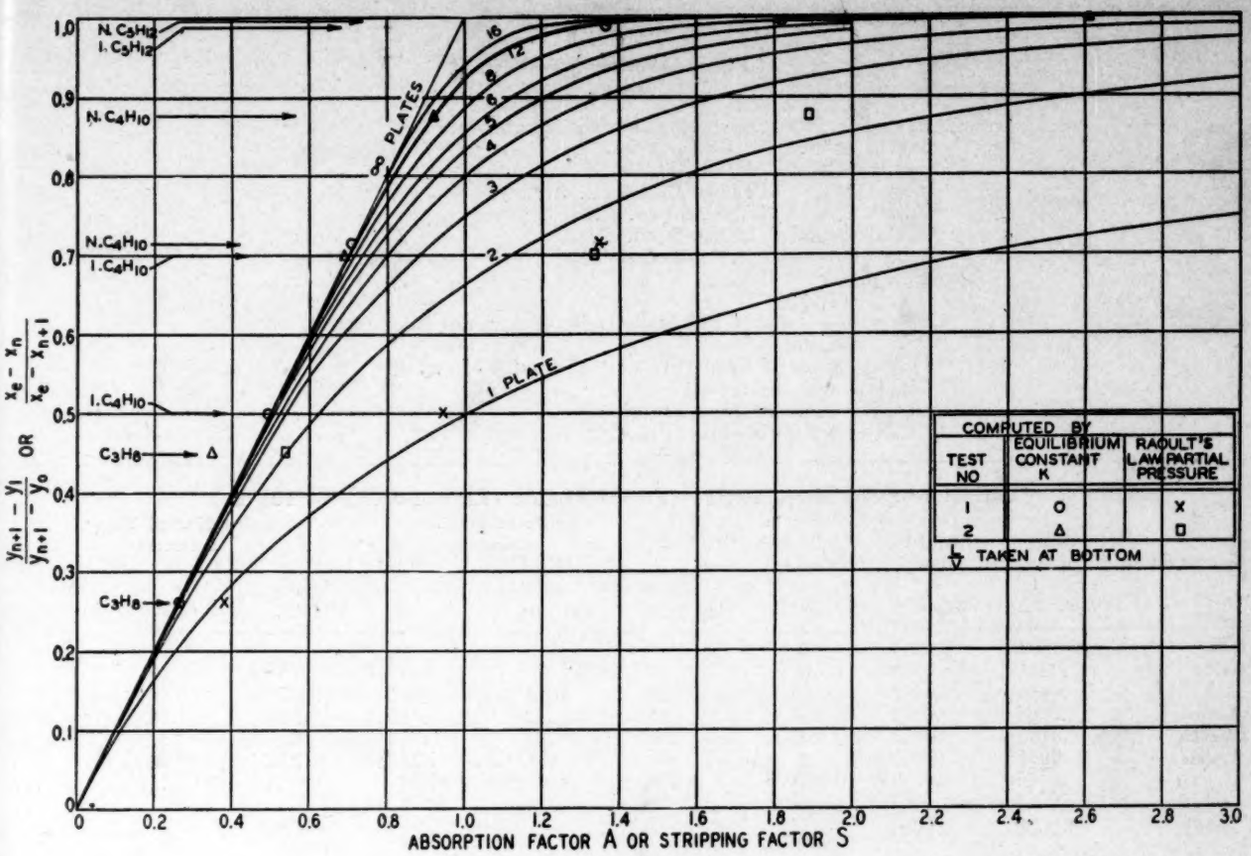



**FIGURE 6**

sumption is sufficiently accurate unless the temperature of the gas is quite different from that of the oil.

In low pressure absorbers operating on rich gases there is sufficient increase in the quantity of oil due to the absorbed components that the oil gas rate at the bottom of the column should be used. Figure 7 shows the results of a plate to plate calculation on actual terminal conditions of an absorber operating at 45 pounds per square inch gauge pressure on a rich gas. The actual absorber contains 10 plates which were found to be equivalent to the five equilibrium plates shown in the figure, thereby indicating a plate efficiency of 50 per cent. Figure 7 shows the composition of the liquid and vapor on each plate and the temperature of the oil on each plate.

The mean effective temperature is practically the arithmetic average of the inlet and outlet oil temperature. The temperature of the oil leaving the absorber may be estimated from plant data or calculated from the latent heat of the absorbed components. In the absence of operating data this requires the assumption of a mean effective temperature for preliminary determination of the quantity of material absorbed. The temperature of the outlet oil is then calculated on the basis of the latent heat of the absorbed components. The mean effective temperature can then be determined more accurately and a second calculation of the absorber is usually sufficient to obtain satisfactory check results.

High pressure absorbers include absorbers operating at all pressures over 100 pounds and require special treatment in some respects. Because of the relatively high absorption at high pressure the oil gas rate at the bottom of the column should be used in determining the absorption factor. It should be kept in mind that the methane is actually absorbed to only about one-half the extent that would be indicated by the equilibrium constants based upon ideal solution when the total pressure is 500 pounds. For this reason the oil rate at the bottom must be corrected for this deviation in the solubility of methane in absorption oil when designing high pressure absorbers. At low pressures the solubility of methane is almost negligible and need not be considered.

Perhaps the most difficult factor to estimate in designing high pressure absorbers is the mean effective temperature to be used in determining the absorption factor. Because of the relatively large amounts of methane and ethane absorbed at high pressures it is not possible to calculate the rise in temperature because of lack of data on the heat of solution of these gases in the absorption oil. For this reason it is necessary at present to rely upon experience in estimating the mean effective tempreature. Usually the mean effective temperature under such conditions may be taken as about 15°F. higher than the temperature of the entering gas. Figure 8 shows the actual temperature distribution in absorbers operating at 470 pounds gauge pressure. In this figure the plates are actual plates and the temperatures actual

**TABLE 3**

**24-Plate Absorber—Test No. 1**

(24 actual plates)

Absorber Pressure 485 lbs./sq. in. absolute
Gas in 88°F. Gas out 94.5°F.
Oil in 69°F. Oil out 105°F.

| | | |
|---|---|---|
| Inlet Gas | 18,780,000 std. cu. ft./day | 49,600 Mols |
| Outlet Gas | 17,700,000 cu. ft. | |
| Gas absorbed | 1,080,000 cu. ft. | 2,850 Mols |
| Lean oil | 111,840 Gal./day | 4,820 Mols |
| Rich oil | | 7,670 Mols |

$$\frac{L}{V} = \frac{7{,}670}{49{,}600} = 0.155 \text{ Mols rich oil per mol inlet gas}$$

Composition of Lean Oil — 161 Mol wt. 0.836 sp. gr.
$iC_5H_{12}$ and lighter—0
$nC_5H_{12}$—0.00073 Mol Fraction
$C_6H_{14}+$—0.00558 Mol Fraction

**MEAN ABSORPTION TEMP. (FROM PLATE-TEMP. DATA) = 105°F.**

| Component | Inlet gas $y_{n+1}$ Mol. Fr. | Outlet gas $y_1$ Mol. Fr. | Vapor in Equil. with Lean Oil at 70° F $y_o$ | From Equil. Constant $\frac{y_{n+1}-y_1}{y_{n+1}-y_o}$ | K 105°F. 485 lbs. | $A=\frac{0.155}{K}$ | From Normal Vapor Pressures $p_n$ 105°F. | $p_n/P$ | $A=\frac{0.155}{p_n/P}$ |
|---|---|---|---|---|---|---|---|---|---|
| $CH_4$ | 0.8302 | 0.8869 | 0 | | | | | | |
| $C_2H_6$ | .0841 | .0688 | 0 | | | | | | |
| $C_3H_8$ | .0476 | .0352 | 0 | 0.26 | 0.59 | 0.263 | 197 | 0.406 | 0.381 |
| $iC_4H_{10}$ | .0084 | .0042 | 0 | .50 | .32 | .485 | 79 | .163 | .951 |
| $nC_4H_{10}$ | .0166 | .0047 | 0 | .717 | .22 | .705 | 56 | .115 | 1.35 |
| $iC_5H_{12}$ | .0061 | .00006* | 0 | .99 | .113 | 1.37 | 22.2 | .046 | 3.39 |
| $nC_5H_{12}$ | .0016 | .00004* | 0.000033 | .996 | .085 | 1.82 | ... | ... | ... |
| $C_6H_{14}+$ | .0054 | .0001 * | ..... | ... | ... | ... | ... | ... | ... |
| Total | 1.0000 | 1.0000 | | | | | | | |

*Estimated from analysis of outlet gas which indicated 0.0002 mol fraction of isopentane plus.

measurements of the temperature in the liquid overflow from each plate.

The complete test data from these absorbers operating with different oil rates serve as an excellent indication of the accuracy of the results obtained from the use of the equilibrium constants as compared with those computed by the assumption of Raoult's Law.

Actual measurements on a 24-plate absorber operat-

**TABLE 4**

**24-Plate Absorber—Test No. 2**

Absorber Pressure 485 lbs. sq. in. abs.
Gas in 77°F. Gas out 82°F.
Oil in 63°F. Oil out 93.5°F.

| | | |
|---|---|---|
| Inlet Gas | 11,084,000 std. cu. ft./day | 29,200 Mols |
| Outlet Gas | 10,290,000 | |
| Gas absorbed | 794,000 | 2,090 Mols |
| Lean oil | 75,480 Gal/day | 3,270 Mols |
| Rich oil | | 5,360 Mols |

$$\frac{L}{V} = \frac{5{,}360}{29{,}200} = 0.185 \text{ Mols rich oil per mol inlet gas}$$

Composition of Lean Oil same as Test No. 1.

**MEAN ABSORPTION TEMP. (FROM PLATE TEMP. DATA) = 93°F.**

| Component | Inlet gas $y_{n+1}$ Mol. Fr. | Outlet gas $y_1$ | Vapor in Equil. with Lean Oil at 65°F. $y_o$ | From Equil. Constant $\frac{y_{n+1}-y_1}{y_{n+1}-y_o}$ | K 93°F 485 lbs. | $A=\frac{0.185}{K}$ | From Normal Vapor Pressures $p_n$ lbs. abs. | $p_n/P$ | $A=\frac{.185}{p_n/P}$ |
|---|---|---|---|---|---|---|---|---|---|
| $CH_4$ | 0.8302 | 0.9096 | 0 | | | | | | |
| $C_2H_6$ | .0841 | .0597 | 0 | | | | | | |
| $C_3H_8$ | .0476 | .0261 | 0 | 0.452 | .053 | 0.349 | 168 | .0.346 | 0.535 |
| $iC_4H_{10}$ | .0084 | .00253 | 0 | .700 | .27 | .685 | 67 | .138 | 1.34 |
| $nC_4H_{10}$ | .0166 | .00202 | 0 | .879 | .20 | .925 | 47 | .098 | 1.89 |
| $iC_5H_{12}$ | .0061 | | | | .093 | 1.99 | 18.2 | .0375 | 4.94 |
| $nC_5H_{12}$ | .0016 | .00005 | .0000285* | .997 | .071 | 2.61 | .... | ..... | .... |
| $C_6H_{14}t$ | .0054 | | | | | | | | |
| Total | 1.0000 | 1.00000 | | | | | | | |

*Evaluated from $C_6H_{14}$ + in lean oil taken as $nC_6H_{14}$.

ing at 470 pounds per square inch gauge in which the mean effective temperature was 105°F. show that 57.5 standard cubic feet of gas were dissolved in 5.95 gallons of lean oil per 1000 standard cubic feet of inlet gas. The lean oil had a molecular weight of 161 and a specific gravity of 0.8363.

The mols of rich oil at the bottom of the absorber per 1000 standard cubic feet of inlet gas were

$$\frac{57.5}{379} + \frac{5.95 \times 8.33 \times 0.8393}{161} = 0.409$$

and the molal oil-gas ratio $\left(\frac{L}{V}\right)$ at the bottom.

$$\frac{L}{V} = \frac{.409 \times 379}{1000} = 0.155 \text{ mols rich oil per mol inlet gas}$$

The mol fraction of normal butane in the inlet gas was 0.0166, in the outlet gas 0.0047, and in the lean oil zero. For normal butane at 485 pounds per square inch absolute and 105°F., the equilibrium constant, K, is 0.22 (from Figure 4).

$$\frac{y_{n+1} - y_1}{y_{n+1} - y_0} = \frac{.0166 - 0047}{0166 - 0} = 0.717$$

$$A = \frac{L}{KV} = \frac{0.155}{0.22} = 0.705$$

These values are the coordinates of a point plotted on Figure 6.

The results of similar calculations for all components above ethane are also plotted in Figure 6. The same absorber when operating with an oil-gas ratio of 6.82 gallons per 1000 cubic feet provided additional points as summarized in Tables 3 and 4.

With the exception of a single point for propane which is without doubt due to an error in analysis, all of the calculated points fall almost exactly on the curve for 12 equilibrium plates indicating an apparent overall efficiency of 50 per cent.

The results of conventional calculations based on Raoult's and Dalton's Laws are also indicated for purposes of comparison. Not only do such calculations indicate unreasonably low plate efficiency of about 8 to 12 per cent but they are inconsistent among themselves.

This comparison clearly shows that Raoult's and Dalton's Laws may not be used for calculating high pressure absorbers; but that the use of the equilibrium constants as outlined above gives reliable results consistent with actual operating data.

## APPLICATION TO DESIGN PROBLEMS

The application of this method to the design of absorbers is indicated by the following example.

An absorber operating at 470 pounds per square inch gauge is to treat 11,084,000 standard cubic feet of gas entering at 77°F. with lean oil of 161 molecular weight and 0.8363 specific gravity. The lean oil, supplied at 65°F. may be expected to be free of iso-pentane and the more volatile components and to contain 0.00073 mol fraction of n-pentane.

It is desired to recover 99.9 per cent of the iso-pentane in the rich gas with 12 equilibrium (24 actual) plates.

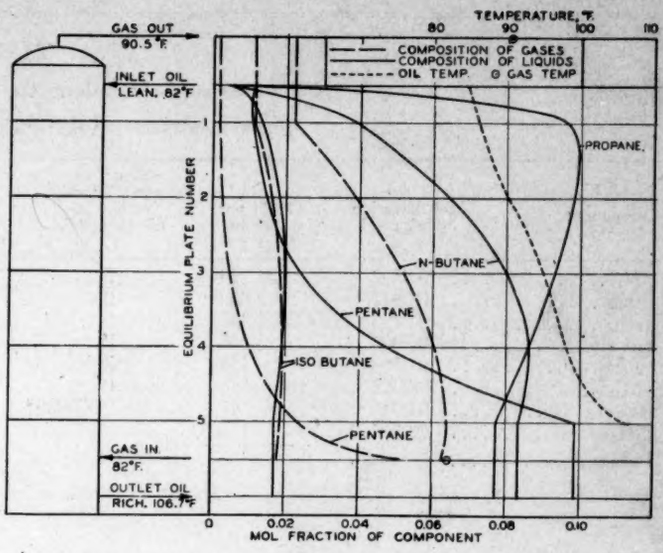



**FIGURE 7**

***Temperature and Composition Distribution in Low Pressure Absorber.***

The mean effective absorbing temperature is taken as 93°F.

For iso-pentane, since $y_0 = 0$

$$\frac{y_{n+1} - y_1}{y_{n+1} - y_0} = 0.999$$

so that from the curve for 12 plates on Figure 6

$$A = 1.99.$$

The absorption factors for the other components may be calculated from the absorption factor of isopentane since the absorption factors vary inversely with the equilibrium constants.

From the known absorption factors, composition of the lean oil, analysis of the inlet gas, and the curve for

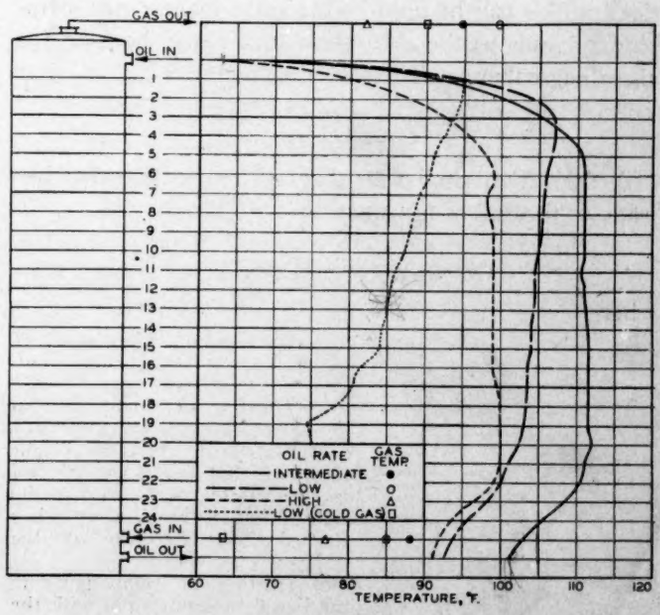



**FIGURE 8**

***Liquid Temperature Gradient in High Pressure Abhorbers***

**TABLE 5**

**Design Calculations for High Pressure Absorber**

Basis 11,084,000 Standard Cubic Feet Inlet Gas Per Day

| Component | Mol Fraction in inlet gas $y_{n+1}$ | Mols per day in inlet gas | Vapor in equilibrium with lean oil at 65°F. $y_0$ | Equil. constant K at 93°F. and 485 lbs. | Absorption factor A at 93°F. and 485 lbs. | $\frac{y_{n+1}-y_1}{y_{n+1}-y_0}$ | Per cent absorbed | Mols per day absorbed |
|---|---|---|---|---|---|---|---|---|
| $CH_4$ . . . . . | 0.8302 | 24,279 | 0 | 2 x 6.4 | 0.0145 | 0.0145 | 1.45 | 352 |
| $C_2H_6$ . . . . . | 0.0841 | 2,460 | 0 | 1.22 | 0.1515 | 0.1515 | 15.15 | 373 |
| $C_3H_8$ . . . . . | 0.0476 | 1,392 | 0 | 0.53 | 0.349 | 0.349 | 34.9 | 486 |
| $isoC_4H_{10}$ . . . . . | 0.0084 | 246 | 0 | 0.27 | 0.685 | 0.685 | 68.3 | 169 |
| $nC_4H_{10}$ . . . . . | 0.0166 | 485 | 0 | 0.20 | 0.925 | 0.877 | 87.7 | 425 |
| $isoC_5H_{12}$ . . . . . | 0.0061 | 178 | 0 | 0.093 | 1.99 | 0.999 | 99.9 | 178 |
| $n\text{-}C_5H_{12}$ . . . . . | 0.0016 | 47 | 0.0000285 | 0.071 | 2.61 | 0.997 | 98.6 | 46 |
| $C_6H_{14}+$ . . . . . | 0.0054 | 158 | | | | | 98.6 | 151 |
| Total . . . . . | | 29,245 | | | | | | 2180 |

$$\frac{L}{V} = KA$$

Using the absorption factor and equilibrium constant for isopentane, at the bottom of the absorber

$$\frac{L}{V} = 0.093 \times 1.99 = 0.185 \text{ Mols rich oil per mol inlet gas}$$

29,250 x 0.185 = 5410 mols rich oil per day
2180 mols absorbed per day
3230 mols lean oil per day required

The gallons of lean oil required per 1000 standard cu. ft. of inlet gas,

$$G = \frac{3230 \times 161}{11{,}084 \times 8.33 \times 0.8363} = 6.73 \text{ lean oil rate required.}$$

12 plates on Figure 6, the mols of each component absorbed from the gas may be calculated. These calculations are summarized in Table 5.

In an actual test under these conditions 6.82 gallons of lean oil per 1000 standard cubic feet of inlet gas were circulated.

## CALCULATIONS FOR STRIPPING COLUMN

By making the same assumptions as for the derivation of the absorption factor, a stripping factor may be derived which can be used in the same manner for stripping columns as the absorption factor may be used for absorbing columns. The stripping factor S is defined as

$$S = K\frac{V}{L}$$

A derivation similar to that applied to the absorber leads to the following equation

$$\frac{x_e - x_n}{x_e - x_{n+1}} = \frac{S^{n+1} - S}{S^{n+1} - 1}$$

where

$x_n$ = mol fraction of component in liquid leaving the bottom plate (n) of the stripper

$x_e$ = mol fraction of component in liquid entering the top plate (1) of the stripper. It is important to realize that this is not the mol fraction of the component in the rich oil but in the oil after it has flashed into the top of the stripper

$x_{n+1}$ = mol fraction of components in the liquid in equilibrium with the stripping vapor.

For convenience it is recommended that $x_e$ be used as the mol fraction in the rich oil and the number of equilibrium plates as computed on this basis be reduced by one in the final design as this procedure is much simpler and sufficiently accurate for all practical purposes.

This corresponds to the plot for the absorption factor (Figure 6) so that the same chart may be used for both absorption and stripping calculations. When used for stripping the ordinate of Figure 6 becomes

$$\frac{x_e - x_n}{x_e - x_{n+1}}$$

and the abscissa, the stripping factor S. In using the chart it should be noted that the stripping factor

$$S = \frac{KV}{L}$$

whereas the absorption factor

$$A = \frac{L}{KV}$$

Ordinarily steam is used for stripping, so that $x_{n+1}$, the mol fraction of the component in liquid in equilibrium with the stripping vapor entering the stripper, equals zero, and the stripping equation reduces to

$$\frac{x_e - x_n}{x_e} = \frac{S^{n+1} - S}{S^{n+1} - 1}$$

In this case the value of the ordinate read from Figure 6 represents the fraction of the original content of any component of the oil which is removed by the stripping operation.

In practice it is customary to express the steam required for stripping as pounds of steam per gallon of

oil. If W represents the pounds of steam per gallon of oil

$$S = \frac{KV}{L} = \frac{KWM}{18 \times 8.33d}$$

As in the design of absorbers, the steam oil rate as determined for the bottom of the stripper is used in determining the stripping factor. The effective stripping temperature is also the temperature existing at the bottom of the stripper. This bottom temperature may be calculated from the latent heat of the material vaporized in the stripper. This material includes not only the gasoline components stripped from the oil but also some of the absorbent oil itself. This may be computed by use of the stripping factor method considering the absorption oil as one component or preferably assuming three or four components to represent the absorption oil based upon the distillation curve of the oil. The values for the equilibrium constants of these components may be determined from Figure 2 in the manner which has already been described.

Simple straightforward methods for calculating the fractionating section are not available and it is still necessary to resort to the trial and error method in which the composition of the overhead and the amount of steam condensed is assumed, the heat balance is then made on the basis of an assumed top temperature thereby fixing the reflux ratio with the material balance. A recalculation is then made to check the quantity of steam condensed. If this agrees with the assumed value the calculations are considered satisfactory otherwise a second trial is necessary.

## GASOLINE FRACTIONATING COLUMNS

Although constant temperature was assumed in the derivation of the equations for the absorption and stripping factors, this method of design is not limited to those conditions where the temperature is actually constant throughout the equipment. The use of a mean effective temperature has been found to give entirely satisfactory results in the design of absorbers and strippers even when the temperature of the oil may vary over rather wide limits throughout the absorber. By use of this same device, a mean effective temperature, the absorption factor method may be extended and used with entirely satisfactory results on fractionating columns where the temperature is far from constant, provided that a reasonably satisfactory method of estimating the mean effective temperature is available.

In fractionating gasolines it is customary to use relatively high reflux ratios so that the absorption factors are numerically larger than those found for absorbing columns. This means that the computed results by means of the absorption factor method are less sensitive to changes in the absorption factor or to errors in estimating the mean effective temperature. Under these conditions it has been found that the mean effective temperature for the absorption or stripping of a particular component may be taken as a straight line function of the ratio $\frac{O}{V}$.

The principles of the method as applied to the fractionation of natural gasoline were published recently.[5] In this paper the method is applied to the fractionation of refinery gasoline using as a particular case a debutanizer operating at 100 pounds pressure.

It is desired to debutanize a refinery gasoline whose composition may be represented as follows:

| Component | Volume % | Mol Fraction |
|---|---|---|
| Butane | 7.2 | 0.1 |
| Pentane | 10.8 | 0.13 |
| Heptane | 82.0 | 0.77 |

so that the stabilized product contains not more than 0.008 mol fraction of butane, and the overhead product not more than 0.016 mol fraction of heptane. This is a sharper separation than is usually demanded for debutanizing equipment, as the overhead product is usually again fractionated closely under a higher pressure. But the sharper separation makes a more effective problem for demonstrating the method.

The pressure at which the column is to operate must be determined by preliminary consideration taking into account the temperature of the cooling water and the necessity of forming adequate reflux for the top of the column. It is impossible to compute these relationships until the composition of the overhead product is known and this in turn can not be determined until after the plant is designed. In this case an absolute pressure of 100 pounds per square inch is considered adequate but should be checked after the composition of the overhead product has been determined.

Before attempting to design the column by means of the absorption factor method it is necessary to know the average effective temperature for each component under consideration. This is best determined by independent calculations based on infinite reflux ratio and on minimum reflux ratio to set the limiting conditions of temperature and evaluate mean effective temperature.

Consider first the heptane in the rectifying part of the column, i.e., above the feed plate. The temperature and the composition of the vapor rising from the feed plate is determined by assuming a temperature and computing the composition of the vapor in equilibrium with the liquid feed by use of the equilibrium constant at the total pressure of 100 pounds per square inch absolute and at the assumed temperature, until the assumed temperature gives a vapor composition such that the sum of the mol fractions is equal to unity. The results of such a computation at the feed plate indicates a temperature of 300°F. and the following composition of the vapors rising from the feed plate which is represented by $y_f$.

| Components | Mol fraction in vapor $y_f$ |
|---|---|
| Butane | 0.298 |
| Pentane | 0.238 |
| Heptane | 0.463 |

Since we are determining the conditions for infinite

[5] Brown, Souders and Nyland—Ind. Eng. Chem. V. 24, p. 522, May 1932.

reflux the composition of the liquid on the plate above the feed plate will be the same as that of the vapor arising from the feed plate, or $y_f = x_{f-1}$.

The vapors rising from plate f—1 are then computed in the same manner and the process continued until a vapor having the desired composition of heptane is obtained. The following tabulation gives the results of these calculations for infinite reflux ratios or when $\frac{O}{V} = 1$.

**TABLE 6**

| Component | $x_f$ 300°F. | $y_f$ or $x_{f-1}$ 230°F. | $y_{f-1}$ or $x_{f-2}$ 173°F. | $y_{f-2}$ or $x_{f-3}$ 153°F. | $y_{f-3}$ or $y_0$ |
|---|---|---|---|---|---|
| Butane | 0.1 | 0.298 | 0.624 | 0.838 | 0.93 |
| Pentane | 0.13 | 0.238 | 0.254 | 0.145 | 0.064 |
| Heptane | 0.77 | 0.463 | 0.125 | 0.016 | 0.00144 |

Applying the absorption factor equation to the operation of the rectifying column which is here regarded as an absorber of heptane the following relationship is obtained.

$$\frac{y_{n+1}-y_1}{y_{n+1}-y_0} = \frac{y_f - y_{-2}}{y_f - y_0} = \frac{.463 - .016}{.463 - .00144} = \frac{.446}{.4606} = .968$$

Since this column is operating with two equilibrium plates above the feed plate the corresponding absorption factor is read from Figure 6 as the intersection of the curve for two equilibrium plates with the ordinates 0.968. The absorption factor so determined is found to be 4.9. This indicates a value for the equilibrium constant of heptane.

$$K = \left(\frac{L}{V}\right)\left(\frac{1}{A}\right) = 0.204$$

The value for $\frac{L}{V}$ under conditions of infinite reflux is unity. This value for K corresponds to a mean effective temperature of 210°F. for infinite reflux.

The other limiting case is when operating with infinite plates or minimum reflux. Under such conditions the reflux ratio may be determined as follows:

$$\frac{L}{V} = \frac{y_f - y_1}{x_f - y_1} = \frac{.463 - .016}{.77 - .016} = \frac{.446}{.754} = .59$$

Having determined the value for $\frac{L}{V}$ in this manner the same equation may be applied to the conditions for the other components in order to determine the mol fraction of the components in the vapor leaving the top of the column. Having determined the composition of the vapor leaving the top of the column and assuming total condensation of this material, part of which is returned as reflux, the mol fraction in the vapor in equilibrium with the liquid reflux $y_0$ may then be computed. The results of these computations are given in Table 7:

**TABLE 7**

| Component | Mol Fraction Vapor $y_1$ or $x_0$ | Mol Fraction Vapor in Equilibrium with Liquid Reflux $y_0$ |
|---|---|---|
| | | 173°F. |
| Butane | 0.583 | 0.77 |
| Pentane | 0.401 | 0.224 |
| Heptane | 0.016 | 0.00195 |

With these values determined it is possible to compute the absorption factor and mean effective temperature for heptane when the column is composed of infinite plates and operating with minimum reflux making an overhead product containing 0.016 mol fraction of heptane. The results of these calculations which are carried out in the same manner as those for infinite reflux indicate an absorption factor of 0.975, an equilibrium constant of 0.605 corresponding to a mean effective temperature of 300°F. for heptane in the rectifying column operating with minimum reflux.

Having determined the two limiting conditions and the corresponding mean effective temperatures 210°F. for infinite reflux, and 300°F. for minimum reflux, the mean effective temperature for heptane in the rectifying column is represented by the following equation

$$\text{Mean effective temperature } °F = 430 - 220\frac{L}{V}$$

Attention should be called at this time to the fact that the temperature at which the overhead vapors may be totally condensed at 100 pounds absolute pressure are well above that usually obtained in such plants. In the case of infinite reflux a temperature of 150°F. will serve to condense substantially all of the overhead vapors. In the case of minimum reflux cooling to a temperature of 173°F. is adequate for this purpose. This is an indication that the pressure is higher than necessary, but the calculations will be continued on this basis.

Considering the rectifying column as a stripper of butane, similar calculations using the stripping factor enables us to compute the mean effective stripping temperature for butane in this part of the column.

For infinite reflux and with two equilibrium plates

$$\frac{x_e - x_n}{x_e - x_{n+1}} = \frac{x_0 - x_{f-1}}{x_0 - x_f} = \frac{.838 - .298}{.838 - 1} = \frac{.54}{.738} = .73$$

From which S is found to equal 1.22, which is also the value of K since $\frac{L}{V}$ is equal to unity at infinite reflux.

From Figure 4 for butane when K = 1.22 the temperature is found to be 162°F.

Similarly for minimum reflux

S = 1

K = .59 which corresponds to a mean effective temperature of 103°F.

Relating the mean effective temperature as a straight line function of the ratio $\frac{L}{V}$

The mean effective temperature in °F $= 18 + 144 - \frac{L}{V}$

Considering the stripping column or that part of the fractionator below the feed plate, for infinite reflux the composition of vapor rising to the feed plate is the same as that of the liquid on the feed plate. The composition of the liquid on the next lower equilibrium plate may be computed by assuming the temperature and computing the mol fraction of the individual components in the liquid, the correct solution being reached when the summation of the mol fractions in the liquid is equal to unity. Following this procedure the results shown in Table 8 were obtained.

**TABLE 8**

| Component | Mol Fraction in liquid on feed plate $x_f$ or $y_{f+1}$ | $x_{f+1}$ or $y_{f+2}$ 335°F. | $x_{f+2}$ or $y_{f+3}$ 345°F. | $x_{f+3}$ 353°F. |
|---|---|---|---|---|
| Butane | 0.1 | 0.0301 | 0.008 | 0.00226 |
| Pentane | 0.13 | 0.059 | 0.025 | 0.0105 |
| Heptane | 0.77 | 0.905 | 0.972 | 0.987 |

It was found that two equilibrium plates below the feed plate will reduce the butane content to 0.8 mol per cent in the overflow from that plate.

Using the same equation for the stripping factor in which $x_e = x_f$, $x_n = x_{f+2}$ and $x_{n+1}, = x_{f+3}$, S is found to have a value of 3.45. Since $\frac{\overline{L}}{\overline{V}}$ is unity, K = 3.45 which corresponds to a mean effective temperature of 345°F.

For minimum reflux the following equation is used to compute the ratio $\frac{\overline{L}}{\overline{V}}$ for the lower part of the fractionating column.

$$\frac{\overline{L}}{\overline{V}} = \frac{y_f - x_n}{x_f - x_n} = \frac{.298 - .008}{.1 - .008} = \frac{.29}{.092} = 3.15$$

Applying this equation to the other components the composition of the liquid leaving the bottom plate of the column is computed as follows

| Components | Mol Fractions $x_n$ |
|---|---|
| Butane | 0.008 |
| Pentane | 0.079 |
| Heptane | 0.913 |

Under conditions of minimum reflux or infinite plates S = 1 and K is equal to 3.15. This corresponds to a mean effective temperature of 320°F.

The mean effective temperature for the stripping of butane in the lower or stripping section of the fractionator is represented by the equation

$$\text{Mean effective temperature °F.} = 356.6 - 11.6\frac{L}{V}$$

A somewhat less convenient but more obvious method of obtaining the ratio $\frac{\overline{L}}{\overline{V}}$ is by means of a material balance as follows

$$x_f = x_D - Bx_D + Bx_B$$

$$\frac{x_f - x_D}{x_B - x_D} = B, \text{ for Butane } \frac{.1 - .583}{.008 - .583} = .84$$

$$D = F - B = 0.16$$

$$L = .59 \quad V = V - D = V - 0.16$$

$$V = \frac{.16}{.41} = .39$$

$$L = .23$$

Since all the feed is liquid

$$\overline{L} = L + F = .23 + 1 = 1.23$$

$$\frac{\overline{L}}{\overline{V}} = \frac{\overline{L}}{V} = \frac{1.23}{.39} = 3.15$$

Under conditions of minimum reflux or infinite plates S is not equal to 1 for the stripping column because the change in composition from plate to plate at the bottom of the fractionator is finite even for infinite number of plates. Therefore $x_n$ is not equal to $x_{n+1}$ at the bottom of the stripper although it is true at the bottom of the rectifier or for the plates immediately above the feed plate when operating at minimum reflux. For this reason it is necessary to compute the composition of the liquid on the plate below the bottom plate of the stripper or $x_{n+1}$.

This computation may be made by drawing off the bottom product from the bottom plate of the column and passing the balance of the liquid overflow from the bottom plate to a heat exchanger or kettle so that the composition of the vapors rising to the bottom plate of the stripping column is the same as that of the liquid overflowing from the bottom plate. This assumption is equivalent to that made at the top of the column where the composition of the liquid reflux returned to the top plate is the same as that of the vapors leaving the top plate. This assumption simplifies the calculations and introduces no serious error in the results, for if the bottom product is to be withdrawn from the kettle instead of from the bottom plate of the column it is simply necessary to include the kettle as one of the equilibrium plates or, more conservatively, as one of the actual plates in the stripping column when converting the number of equilibrium plates to actual plates required.

On this basis the composition of the liquid in the kettle was determined as follows:

| Component | Mol and mol fraction in liquid on plate below the bottom plate $x_{n+1}$ @ 348 °F. |
|---|---|
| Butane | .0023 |
| Pentane | .0339 |
| Heptane | .961 |

Using the stripping factor equation and Figure 4 for infinite plates we find that S = 0.95, and that K = 2.99 corresponding to a temperature of 305°F. for the stripping factor of butane in the stripping section of the column.

The mean effective temperature for butane in the stripping section is represented by the equation

$$T°F. = 363.6 - 18.6\frac{\overline{L}}{\overline{V}}$$

By use of these relationships between the mean effec-

**TABLE 9**

**Results of Design Calculations for Gasoline Fractionator**

| Molal Reflux Ratio $\frac{L}{D}$ | Feed | Overhead Product Rectifying Column | | | | Bottom Product Stripping Column | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | ∞ | 5.65 | 2 | Minimum = 1.44 | ∞ | 5.65 | 2 | Minimum = 1.44 |
| Mean Effective temp. $C_4H_{10}$ | | 162°F. | 140°F. | 114°F. | 103°F. | 345°F. | 333°F. | 324°F. | 320°F. |
| Mean Effective temp. $C_7H_{16}$ | | 210° | 243° | 282° | 300° | | | | |
| Mean Effective K $C_4H_{10}$ | | 1.22 | .96 | .7 | .59 | 3.45 | 3.32 | 3.23 | 3.15 |
| Mean Effective K $C_7H_{16}$ | | .204 | .32 | 0.5 | .605 | | | | |
| Absorption or Stripping factor $C_4H_{10}$ | | 1.22 | 1.13 | 1.045 | 1.0 | 3.45 | 1.67 | 1.15 | 1.0 |
| Absorption or Stripping factor $C_7H_{16}$ | | 4.9 | 2.66 | 1.34 | .975 | | | | |
| Equilibrium Plates above, or below, feed Plate* | | 2 | 3 | 7.5 | | 2 | 4.5 | 10 | ∞ |
| Total Equil. Plates in Entire Column* | | 5 | 8.5 | 18.5 | | 5 | 8.5 | 18.5 | ∞ |
| Temp. of Material Entering or Leaving Column | 300°F. | 173°F. | 177°F. | 193°F. | 195°F. | 346°F. | 333°F. | 337°F. | 338°F. |
| Mol % $C_4H_{10}$ | 10.0 | 83.8 | 70.5 | 60.4 | 58.3 | 0.8 | 0.8 | 0.8 | 0.8 |
| Mol % $C_5H_{12}$ | 13.0 | 14.5 | 27.9 | 38.0 | 40.1 | 2.5 | 10.7 | 8.5 | 7.9 |
| Mol % $C_7H_{16}$ | 77.0 | 1.6 | 1.6 | 1.6 | 1.6 | 97.2 | 88.5 | 90.7 | 91.3 |
| Total Mols | 1.0 | 0 | .132 | .154 | .16 | 0 | .868 | .846 | .84 |

*If the Bottoms are removed from the kettle instead of the bottom plate the number of plates in the stripper is reduced by one.

tive temperatures and the $\frac{L}{V}$ ratio, the absorption factor method may be used to determine the number of equilibrium plates and the compositions of the overhead and bottom products obtained with different reflux ratios when separating the specified feed into an overhead product containing not over 1.6 mol per cent of heptane and a bottom product containing not more than 0.8 mol per cent of butane. The detail method of such calculations are the same as for absorbers and strippers already described. Comparative results obtained from such calculations are given in Table 9.

Although this method when applied to calculation of fractionating columns is not so simple as when applied to absorbers or strippers, due to the preliminary calculations for determining the mean effective temperatures, it is the only satisfactory method for computing the number of plates and composition of products for multiple component mixtures under different operating conditions known to us at present. Further work will probably provide simpler ways of estimating the mean effective temperatures.

The same procedure is followed in the case of more complex mixtures which offer no particular difficulty.

As has been indicated by the analysis of actual operating data on high and low pressure absorbers, the overall plate efficiency of well designed absorbers is usually about 50 per cent. It is our experience that the plate efficiency of gasoline fractionators is of about the same order of magnitude (45 to 60 per cent).

Columns operating on heavier distillates frequently show lower plate efficiencies.

This method which treats each individual component independently is particularly well adapted to mixtures of diverse materials where the plate efficiencies for the different components of the mixture may differ and an overall plate efficiency may not be used. Such mixtures are not frequently encountered in the petroleum industry.

## CALCULATION OF COLUMN CAPACITY

So far we have considered only the number of plates required to accomplish a specified purpose. But an equally important problem at least is the computation of the necessary diameter and spacing of the plates.

If sufficient care is taken to provide ample capacity in the downtakes to handle the maximumu flow of liquid down the column; the entrainment of liquid particles in the rising vapor stream is the factor which limits the capacity of the column proper.

The mass velocity of a rising gas stream that will support a liquid particle of definite size is represented by the following equation

$$v = C\,[d_2\,(d_1 - d_2)]^{\frac{1}{2}}$$

$v$ = mass velocity in pounds per hr, per sq. ft. of cross sectional area
$d_1$ = density of vapor in lbs. per cu. ft.
$d_2$ = density of liquid in lbs. per cu. ft.
$C$ = factor dependent upon size of drop which is determined by plate spacing, surface tension of liquid and other factors such as relative quantity of entrainment.

The approximately correct values of C for different conditions are shown in Table 10 as determined from operating data.

**TABLE 10**

**Proper Values to Use for C in Entrainment Equation**

| Distance Between Plates inches | Proper Value for C: No Observable or negligible entrainment Absorbers | Proper Value for C: Allowable Entrainment for Strippers, Fractionators, etc. | Relative Values h |
|---|---|---|---|
| 16 | 250 | 384 | 0.64 |
| 18 | 288 | 444 | 0.74 |
| 20 | 316 | 485 | 0.81 |
| 22 | 340 | 520 | 0.87 |
| 24 | 355 | 545 | 0.91 |
| 30 | 390 | 600 | 1.0 |

## ABSORBERS

Any appreciable entrainment carried over with the lean gas from absorbers represents a direct loss of oil and trouble due to oil in the gas line. For these reasons absorbers are designed and operated on the basis of no

detectable entrainment and the lower values for C as given in the second column are used.

When operating on normal gases and using an oil of assumed constant at about 51. The vapor density $d_2$ 35 to 45°A.P.I. the expression $(d_1—d_2)$ may usually be $= \frac{MP}{zRT}$

M = Molecular weight
P = Absolute Pressure lbs. per sq. in. abs.
z = Compressibility factor Figure 1
R = 10.71
T = absolute temperature (°F.+ 460)

The simplified equation for absorbers under these conditions becomes

$$v = 850\ h \sqrt{\frac{MP}{zT}}$$

or in terms of standard cubic feet of gas per day

$$Q = 7{,}750{,}000\ h \sqrt{\frac{P}{zMT}}$$

Q = No. of standard cu. ft. of gas at 60°F. and 14.6 lbs. per sq. in. per sq. ft. of cross sectional area per 24 hrs.

## RECTIFIERS AND STRIPPERS

A small amount of entertainment is not objected to when it is not responsible for a loss and is present in such a limited amount as to have a negligible effect on the product.

Under such conditions the general equation becomes

$$v = 600\ h \sqrt{d_2(d_1—d_2)}$$

If the density of the liquid is assumed constant at 30 pounds per cubic foot as is the case in the upper trays of many rectifiers,

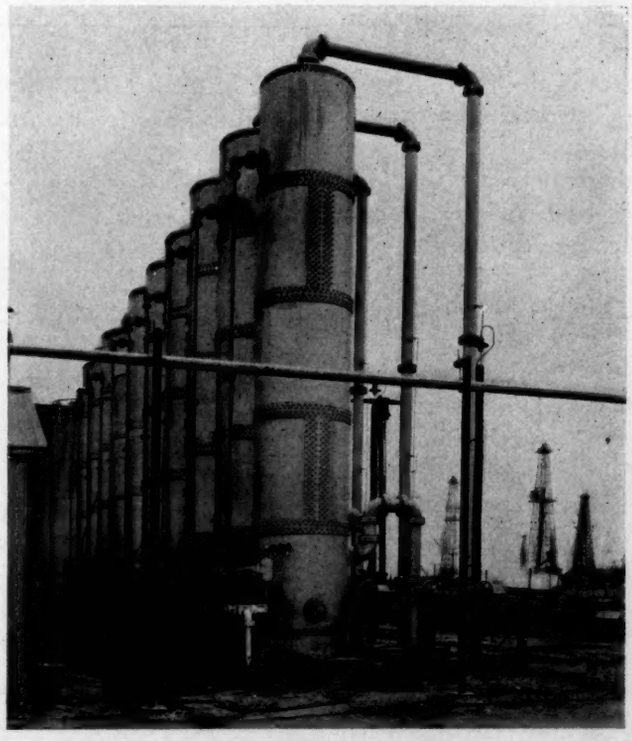
$$v = 1000\ h \sqrt{\frac{MP}{zT}}$$

It should be noted that the vapor load used to compute the mass vapor velocity should include the overhead product, internal reflux, and steam. Since the maximum vapor load is usually just below the top plates in a column it is usually sufficient to determine the vapor load at this point only. But where a greater load may be expected elsewhere in the column calculations should be made to determine the maximum vapor load in order to insure satisfactory operation.

## CONCLUSION

The usual assumption of Dalton's and Raoult's Laws introduces such large errors when used with adequate design formulas that these convenient assumptions must be abandoned except for mere qualitative calculations. The assumption of ideal solutions gives satisfactory results within reasonable limits although small errors are involved.

The use of equilibrium constants determined on the basis of ideal solutions and the deviations from ideal gases has been explained and demonstrated. Simple and accurate methods for the design of absorbers, strippers and rectifiers for multiple components have been demonstrated and found entirely satisfactory when checked against the best plant data now available.



*A Modern Absorption Installation*

# *Notes on . . .*

# Oil-Gas Conversion

**Part 1**

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**THIS is first of a series of articles dealing with oil-gas conversion. The broad, general concept is here laid, to be followed with details of experiment, results of research, and operating data. To those interested in the possibilities of synthesis of natural gas and oils, the accompanying work will be intensely interesting.**

**The ground work, or introductory article for this series on oil-gas conversion, oxidation, synthesis, was presented by Mr. Beall in the Refiner of December, 1931, page 94, "Oxidation of Natural Gas Hydrocarbons." The accompanying discussion carries the work much further, and discusses the effects of time, temperature, pressure, methods of contact and reaction agents.**

ONE of the present major trends in refinery development is toward production of higher anti-knock motor fuels. Automotive engineers are increasing the compression ratio in order to gain fuel efficiency and obtain better performance. The ideal high compression motor fuel should meet two major requirements: (1) it should have a high anti-knock value (2) it should not deposit carbon on explosion in the cylinder. Carbon is a more serious difficulty in the case of high compression motors where the clearance is small than on low compression motors where the clearance is relatively large.

Straight run gasolines vary in anti-knock and carbon producing qualities according to the crude oil from which they are distilled and the method and degree of distillation and refining to which subjected. Cracked gasolines also vary somewhat in the same manner but the most influential factor in determining their characteristics is the type of process used for their conversion. Cracking processes are broadly classified as liquid-phase or vapor-phase. Most processes fall intermediate between the two, that is cracking is part liquid-phase and part vapor-phase. Vapor-phase processes are generally conceded to produce gasoline of higher anti-knock value than liquid-phase processes, but at a sacrifice in yield.

When the gasoline is skimmed from a crude there remains a residue oil. Similarly when the gasoline is stripped from a natural gas there remains a residue gas. Some crudes contain no gasoline, some natural gases contain no gasoline. The crude residue is heavier than gasoline, the stripped natural gas in lighter than gasoline. In such locations where both crude and natural gas are both readily available in quantities and the situation as to markets is strategic, it would seem desirable to have a process which could be used to convert the two simultaneously into motor fuel. This should be particularly true if the cost of production could be kept down and the quality and yield improved. Oil-gas conversion has the aforementioned for its objective.

## PREPARATION OF NATURAL GAS

Natural gas hydrocarbons belong to the chemically saturated series and are not directly capable of combining with oil under heat and pressure unless put into a more active form. An intermediate agent is necessary. Oxygen combines with hydrogen or with carbon. It also enters into chemical combination with the hydrocarbons. The hydrocarbons of natural gas are simple in structure and few in number as contrasted with crude oil or its commercial fractions, such as gas, oil, kerosene, residuum, etc. In conducting chemical reactions it is always advantageous to know the nature of the raw materials and their composition, so it is logical that the primary oxidation should be from the natural gas side rather than the oil.

In order to arrest the oxidation of a natural gas or one of its fractions at some stage short of water, carbon dioxide and carbon monoxide, it is necessary to have carefully controlled conditions. First, the oxygen and hydrocarbon must be somewhat in stoichometric proportions to each other. The time, temperature, pressure, method of contact and reac-

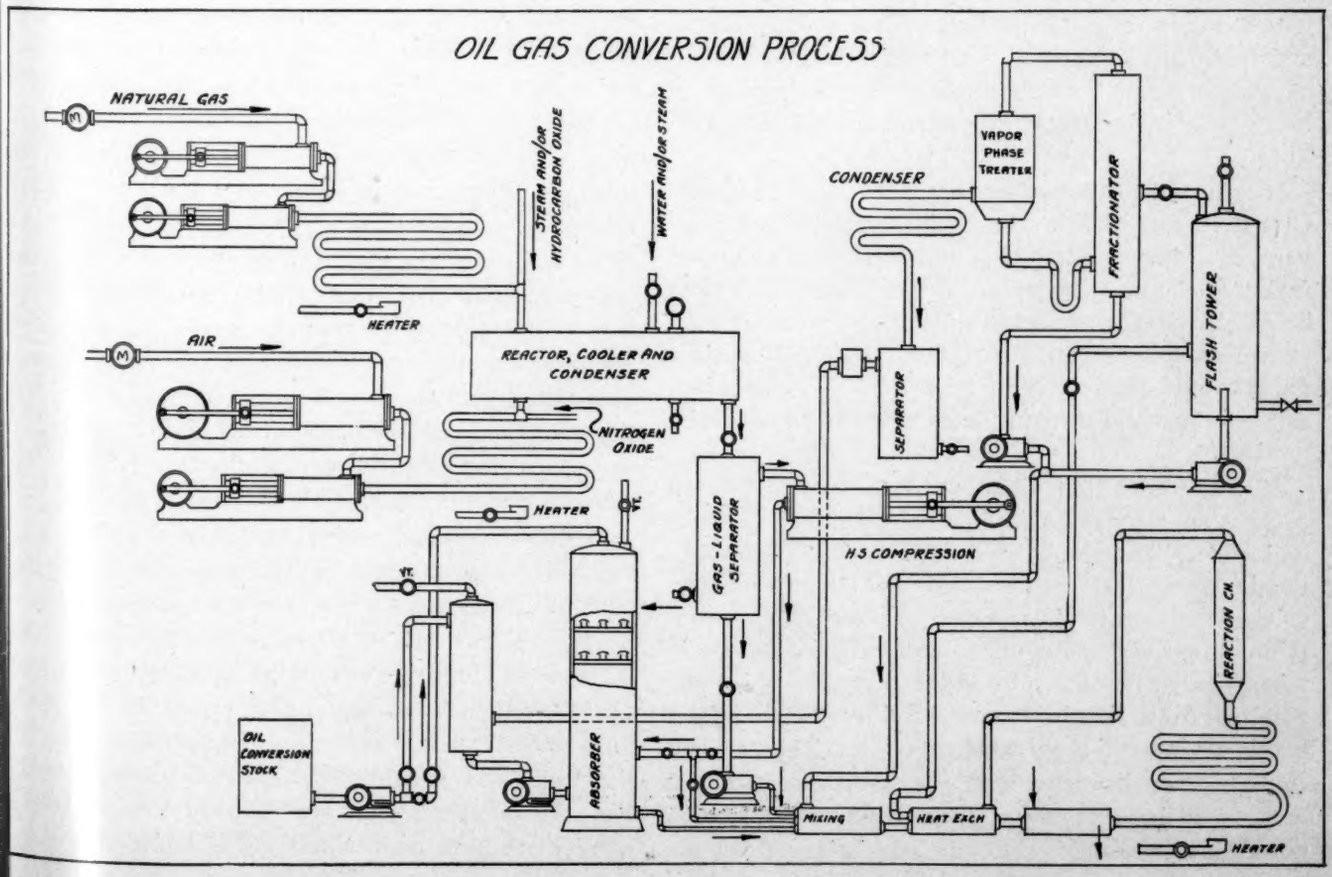
tion promoting agent must also be controlled. The oxidation reactions are strongly exothermic and unless the heat is rapidly dissipated decomposition rather than synthesis takes place.

In order to avoid side reactions taking place on the metal walls of the heating element, the hydrocarbon and oxidizing gas must be heated separately and then contacted within the reaction zone. Shock compression of a mixture of hydrocarbon gas and oxidizing gas within the cylinder of a compressor accomplishes somewhat the same purposes by the temperature rise caused by partially adiabatic conditions. But the mechanical application to large scale production is difficult and the control of temperature, time, pressure and cooling almost impossible. High compression ratios are essential to appreciable temperature rise although results may be obtained by a heated suction line. Better results may be secured by compressing the oxidizing gas and the hydrocarbon gas separately, heating the compressed gases separately after compression to a temperature where, when admixed in the contact zone, reaction will take place. In this way the mechanical difficulties are avoided. If air is used as the oxidizing gas, the promotion agent which may be an oxide of nitrogen is injected into the air line just prior to the inlet to the reaction zone. If added to the natural gas it is probable that it would be used up before the main reaction zone and thereby lose its effectiveness.

## PRODUCTS OF NATURAL GAS OXIDATION

The end products of all such oxidation reactions between natural gas and oxygen are carbon dioxide and water. However in an insufficiency of oxygen for complete combustion hydrocarbon oxides are formed, some of which may be oil-soluble, others of which are water-soluble. Under conditions other than that of very close control using pure or nearly pure constituents, the products of partial oxidation separate into two layers, a water-soluble layer beneath and an oil-soluble layer above. The water-soluble and oil-soluble layers are both complex mixtures consisting of aldehydes, ketones, alcohol, unsaturates, polymerized compounds, etc. Water also, as a rule, results with some free hydrogen and carbon. Portions of these layers may be drawn off and subjected to fractional distillation for the recovery of one or more of the components. However, as the demand for such products as may be contained in the products of natural gas oxidation are somewhat limited, with the exception of motor fuel, these layers are combined and admixed with a predetermined quantity of oil and then subjected to conversion by heat and pressure for the production of motor fuel. These products could be processed separately to produce motor fuel or other materials for which there are established markets. The most promising outlet, however, would seem to be as motor fuel.

Among the probable reactions which take place



on the oxidation of natural gas hydrocarbons the following may be taken as illustrative:

(1). Saturate into unsaturate

$$2\ C_n H_{2n+2} + O_2 \rightarrow 2\ C_n H_{2n} + 2\ H_2O$$

(2). Saturate into aromatic

$$C_n H_{2n+2} + 2O_2 \rightarrow C_n H_{2n-6} + 4H_2O$$

(3). Saturate into aldehyde

$$2\ C_n H_{2n+2} + 2O_2 \rightarrow C_n H_{2n+1} CHO$$

(4). Saturate into carbon and water

$$C_n H_{2n+2} + NO_2 \rightarrow C_n + n\ H_2O$$

and

$$C_n + n\ H_2O + H_2 \rightarrow C_n H_{2n+1} OH$$

The mechanics of oxidation reactions are somewhat complicated as the possibilities of side reactions such as polymerization and condensation are practically unlimited. The main object insofar as oil-gas conversion is concerned is to prepare a maximum quantity of liquid product of oxidation from natural gas. This liquid product is then processed by means of heat and pressure to form a conversion product intermediate between the two.

## HYDROCARBAN OXIDES AND OIL

The beneficial effects of easily reducible metallic oxides has been noted by previous investigators, A. S. Ramage, (U. S. Patent 1,224,787, May 1, 1917) noted the beneficial effects due to the passage of oil vapors over easily reducible metallic oxides. The product of these oxidation reactions is claimed to be rich in the aromatic series. Straches and Porges (U. S. Pat. 1,205,578, Nov. 21, 1916) passed heavy hydrocarbon vapors in the presence of steam over an oxygen "transfer material" and claim to have obtained increased yields of light hydrocarbons. These and many other patents deal with processes where oxygen in some form is used in the conversion of heavy oils in lighter hydrocarbons of greater volatility.

It occurred to the writer that if oxygen were such an active material in the transformation and conversion of heavy oils into lighter oils such as motor fuel, that the most logical form for its addition would be as a hydrocarbon oxide as it added no inert substance requiring regeneration. The hydrocarbon oxide would thus of itself be a part of the conversion mixture and contribute its share to the finished product.

It was found that when alcohols were subjected to heat and pressure in bombs, profound changes took place. The alcohol was no longer the same but two layers separated, one oil-soluble, the other water-soluble and containing water. Other oxygen-containing organic compounds were tried with somewhat similar results. In short, complex mixtures resulted from simple compounds by heating in a bomb under self generated pressure. The oxygen-containing hydrocarbons were evidently a potential but expensive cracking stock from which liquids possessing some of the characteristics of motor fuels could be produced. Fractions of the cracked product could be said to resemble gasoline insofar at least as distillation range was concerned.

On admixture of the higher alcohols with crude oil fractions and heating in a bomb under variable conditions evidence was obtained that a conversion between the two took place. With gasoline and alcohol, reactions were also noted. Oxygen in the combined form seemed to be a desirable constituent in mixtures of hydrocarbon material undergoing conversion due to heat addition. The nature of the final product of heating under pressure would vary in each case not only in accord with the time, temperature and pressure but also with characteristics of the mixture used.

## CONVERSION IN THE VAPOR PHASE UNDER PRESSURE

The critical temperature of a mixture is determinded by the critical temperatures of the components. At temperature above the critical the liquid phase cannot exist. Therefore, if vapor phase is to be produced under pressures higher than the critical pressure and below that of decomposition where tar and carbon deposit, the critical temperature must be lowered for the mixture to a point below that where appreciable cracking occurs.

Heavy oils admixed with hydrocarbon oxide undergo conversion at lower temperatures than would normally obtain in cracking. If such a mixture is subjected to a gradual temperature rise by passage through a sufficient length of tube where the exterior heat conditions surrounding the tubes give a small temperature difference, gradual conversion will take place in the presence of an inert gas such as nitrogen. The average volatility and the average critical temperature will be lowered until vapor phase is produced, regardless of the pressure on the system. After the vapor phase has been produced then the temperature may be raised to the point where maximum conversion into the desired products are obtained. For the production of motor fuel this will be around 1200 pounds or higher and 785°F. or higher, depending upon the characteristics of the mixture and the amount of conversion desired.

Of the two broad general methods of cracking oil, vapor phase and liquid phase, vapor phase operates at high temperatures and low pressures, but produces a motor fuel of high anti-knock value. The increase in quality is somewhat offset by low yields. On the other hand liquid phase and mixed phase high pressure processes are said to produce a higher yield of lower anti-knock value. Oil-gas conversion has the advantage of the two in that yield and quality are both maintained and in addition a cheap

raw material in the form of natural gas is also utilized.

## TAR AND CARBON FORMATION

In the cracking of oils by means of heat at various degrees of pressure, heavy tarry materials form and carbon or low hydrogen, high molecular weight, hydrocarbon deposit. The action of oxygen confined within a cracking system in admixture or in combination as hydrocarbon is to reduce carbon formation. As is well known, air blowing a mass of heated oil residuum is a means for conversion to asphalt but the conditions within a closed continuous system are not comparable. In the manufacture of asphalt, most of the oxygen combines directly with the hydrogen-forming steam which is removed from the system as such. The removal of the hydrogen from the already heavy residuum produces a high degree of unsaturation and chemical activity causing polymerization resulting in sticky viscous asphalt compounds.

In a continuous system where the oil is forced together with hydrocarbon oxide through externally heated tubes under pressure, the oxygen tends to attach itself to the carbon rather than the hydrogen and the reverse of polymerization takes place. In other words, on disintegration the tendency is at least equally toward the formation of carbon dioxide and carbon monoxide. Such a system may be considered as that of carbon, oxygen and hydrogen in shifting equilibrium where every stage of oxidation may exist at least momentarily. The oxygen cannot escape, therefore it enters into chemical combination.

The oxygen-containing hydrocarbons on decomposition have small tendency to deposit carbon. For example, alcohols burn without carbon deposition. On cracking, alcohols, ketones, etc., do not deposit tarry material to the extent as do the saturated, unsaturated and napthene hydrocarbons. In the vapor phase under pressure the tendency toward carbon and tar formation is reduced to a minimum.

The gaseous products from the cracking of hydrocarbon oxide consist of the saturated and unsaturated hydrocarbons together with the oxides of carbon, and free hydrogen. Water may or may not be formed depending upon the conditions maintained during the pyrogenesis. The gaseous products are much reduced over that of ordinary cracking when hydrocarbon oxides are admixed with hydrocarbon oils and subjected to conversion under mechanically applied pressure. The conversion into motor fuel is benefited by the admixture of hydrocarbon oxide.

At low pressures in the presence of what may be termed dehydrating catalysts, the hydrogen and oxygen unite to form water, leaving an unsaturated hydrocarbon or a molecule of lower oxygen content. Thus alcohol may break down to form water and ethylene or at a lower temperature ethers may form in accordance with the following reaction.

$$2\ C_2\ H_5\ OH \rightarrow C_2\ H_5\ OC_2\ H_5 + H_2O$$

The ether is then at higher temperature converted into the unsaturate, ethylene as follows:

$$C_2\ H_5\ O\ C_2\ H_5 \rightarrow 2\ C_2\ H_4 + H_2O$$

or under pressure,

$$C_2\ H_5\ O\ C_2\ H_5 \rightarrow C_4\ H_8 + H_2O$$

An ether or an alcohol may unite with a saturated hydrocarbon with the elimination of water to form a higher saturate

$$C_2\ H_5\ OH + C_2\ H_7 \rightarrow C_4\ H_{10} + H_2O$$

An aldehyde may combine directly with a saturated hydrocarbon

$$CH_3\ CHO + C_2\ H_6 \rightarrow C_3\ H_7\ CH_2\ OH$$

Oxygen is an extremely thermolabile element in the presence of carbon and hydrogen compounds. All theories as to the oxidation must be limited to the conditions of pressure and temperature on a system. The concept of the hydrocarbon molecule is that the hydrogen atoms are attached to the carbon atoms, the carbon atoms being more or less central. At low pressures the oxygen would logically come first in contact with the hydrogen atoms and form water or hydroxyl compounds even though the affinity for the carbon were stronger. On being forced into closer proximity by increased pressure the tendency would be to unite to form an oxygen-containing hydrocarbon which at higher temperature would disrupt, forming carbon monoxide, carbon dioxide, hydrogen and hydrocarbons of lower molecular weight. The formation of carbon would be minimized by the presence of oxygen in the system and carbonization of tubes would not result to the extent that it does in oil cracking. In the vapor phase under pressure the carbon that would form on the disruption of the molecule would be in the finely divided state, and in its nascent condition would combine with the oxygen present. The carbon monoxide is of itself chemically active toward the hydrocarbons and towards hydrogen and would re-enter into combination. The reactions of disintegration and synthesis must take place, the most active element would probably be oxygen in either the free or combined form.

We would then have a conversion system of high flexibility where pressure and temperature could both be modified so as to produce a desired product. If the product is to be rich in aromatics of the benzene series, temperature and pressure should both be elevated. At lower temperature and higher pressure the oxygen-containing hydrocarbons would predominate over that of high temperature and high pressure.

## POSSIBLE REACTIONS OF HIGHER HYDROCARBONS WITH OXYGEN

The affinity between carbon and oxygen is stronger than that between hydrogen and oxygen, as re-

gards heat. While no attempt will be made to substantiate any reaction used as illustration, as oil-gas conversion reactions, similar to cracking reactions are too complicated to analyze, a probable explanation is perhaps desirable. Suppose for example, that a hydrocarbon has an empirical molecular formula corresponding to

$$C_n H_{2n-4}$$

A reaction could be written using a specific molecular weight

$$C_{20} H_{36} + O_2 \rightarrow 2\ C_9 H_{18} + 2CO$$

or

$$C_{20} H_{36} + 2H.\ CHO \rightarrow 2\ C_{10} H_{20} + 2\ CO$$

The CO could then combine with any free hydrogen or with other active hydrocarbons

$$CO + H_2 \rightarrow H.\ CHO$$

or

$$CO + 2\ H_2 \rightarrow CH_3\ OH$$

as the simplest illustrations. Under any condition the elimination of carbon as an oxide of carbon would be preferable to its deposition on the tubes. A reaction chamber exterior to the zone of external heating offers opportunity for the reactions initiated to go to completion. In the example given for $C_{20}H_{36}$ where two carbon atoms are lost as CO the loss in weight would be nine per cent. This would be on the assumption that CO did not re-enter into combination with other hydrocarbon or hydrogen. The decrease in specific gravity would probably cause an increase in volume in the ratio of $\frac{0.850}{0.780} = 1.09$ so that the loss would be compensated on a volumetric basis and a 100 per cent by volume yield would result. In addition the natural gas and hydrocarbon oxide would contribute to increase the overall yield and the overall efficiency based on the oil used.

This article is intended as an introduction to some of the principles of oil-gas conversion. The process, which will be discussed in greater detail in subsequent articles is covered under U. S. Pat. 1,859,193, May 17, 1932, and pending applications.

# *Elimination of* Sulphur Dioxide Nuisance in Light-Oil Sludge Separation

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***(Before A. P. I. Mid-Year Meeting)***

ONE of our eastern refineries is situated in a thickly populated district which makes it imperative to keep all fume nuisances at a minimum. For a number of years acid sludges from treatment of light oils and naphthas were handled as follows:

During a day's operation the acid sludge was run into a cone bottom tank which already contained sufficient water to produce separated acid of the desired gravity. The acid sludge and the water were then agitated with low-pressure air for a few minutes. After a settling period, a fairly good separation of acid, tar, and acid oil could be made.

During the air agitation, large amounts of sulphur dioxide were evolved, and the fact that the sulfur dioxide was practically evolved all in the space of a few minutes made its disposal a troublesome matter.

### SEPARATION OF ACID, TAR, AND ACID OIL

It is well known that fresh light-oil sludges can be treated with water and separated with practically no evolution of sulfur dioxide, and the following scheme was devised in order to make use of this fact. A small tower 10 inches in diameter and 24 feet high was constructed of antimony lead. Acid sludge and water are continuously delivered into the bottom of the tower along with air for agitation. The mixture of sludge and water is discharged at a point about 3 feet below the top of the tower, from which the mixture flows by gravity into one or the other of the two alternately used separating tanks. A period of about 12 hours is allowed for settling; and a good separation of acid, tar, and acid oil is obtained.

Regulation of the water supply to the tower is obtained by occasional gravity determinations made upon samples of separated acid obtained from a small settling drum into which samples of sludge and water can be tapped directly from the tower.

The tower whose dimensions have been given will handle about 16 barrels per hour of combined acid sludge and water. In cold weather it is sometimes necessary to heat the water before mixing with the sludge.

The use of the device described has completely eliminated the fume nuisance connected with the old method of handling acid sludge; and, in addition to this, a cleaner separated acid is obtained. It is, of course, obvious that this method is adapted for use only with sludges that are quite fluid in nature.